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## (54) INK JET RECORDING PAPER AND INK JET RECORDING METHOD USING THE PAPER

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To form a high quality image of high ink absorption properties, high glossiness and high transparency in the aqueous ink printing.

**SOLUTION:** A recording paper is constituted of at least two space layers containing solid fine particles and a hydrophilic binder formed on a substrate. In that case, the average particle diameter of the solid fine particles (A) contained in a space layer on the side far from the substrate is smaller than the average particle diameter of the solid fine particles (B) contained in a space layer on the side close to the substrate, and the total of the space volume of the space layers is 20ml/m<sup>2</sup> or larger.

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CLAIMS

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[Claim(s)]

[Claim 1] The ink-jet record form characterized by for the mean particle diameter of the solid-state particle (A) contained in the opening layer of the side separated from the base material in the ink jet record form which comes to prepare at least the two-layer opening layer containing a solid-state particle and a hydrophilic binder on a base material to be smaller than the mean particle diameter of the solid-state particle (B) contained in the opening layer of a side nearer than a base material, and for the sum total of the void volume of said opening layer to be two or more 20 ml/m.

[Claim 2] The ink jet record form according to claim 1 characterized by said base material being a hydrophobic base material.

[Claim 3] The ink jet record form according to claim 1 or 2 with which said solid-state particle (A) is characterized by being a silica system particle with a mean particle diameter of 7-30nm.

[Claim 4] The ink jet record form according to claim 1 or 2 characterized by being the calcium-carbonate particle said whose solid-state particle (A) is the mean particle diameter of 10-50nm.

[Claim 5] The ink jet record form according to claim 1 or 2 characterized by being the alumina or hydrated alumina particle said whose solid-state particle (A) is the mean particle diameter of 10-100nm.

[Claim 6] An ink jet record form given in any 1 term of claims 1-5 to which said solid-state particle (B) is characterized by being a silica system particle with a secondary [ an average of ] particle size of 1-10 micrometers.

[Claim 7] An ink jet record form given in any 1 term of claims 1-6 characterized by at least one sort of said hydrophilic binder being polyvinyl alcohol or cation denaturation polyvinyl alcohol.

[Claim 8] The ink jet record approach characterized by printing on the conditions from which the amount of maximum regurgitation ink becomes any 1 term of claims 1-7 with two or more 20 ml/m using the ink jet recording ink which contains water soluble dye in the ink jet record form of a publication.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Field of the Invention] This invention relates to the ink jet record approach using the ink jet record form and this which were excellent in ink absorptivity and glossiness in more detail about the ink jet record approach using the ink jet record form and this which record using water color ink.

#### [0002]

[Description of the Prior Art] although ink jet record makes the minute drop of ink fly by various working principles, and is made to adhere to record sheets, such as paper, and an image, an alphabetic character, etc. are recorded, a high speed, the low noise, and multiple-color-izing are comparatively easy — etc. — it has the advantage. About the blinding of a nozzle and the maintenance which had become a problem from the former by this method, from both sides of ink and equipment, amelioration progresses and it has spread through various fields, such as various printers, facsimile, and a computer terminal, quickly in current.

[0003] As an ink jet record form used by this ink jet recording method, also when a printing dot laps [ that a color tone is brightly skillful and absorption of ink ] early, the diffusion to the longitudinal direction of ink flowing out or not spreading and a printing dot is not large [ the concentration of a printing dot is high, and ] beyond the need, and it is required that the circumference should be smooth and should not fade etc.

[0004] Since it becomes nonuniformity, and the color of each other in the border area of a color which a drop causes a HAJIKI phenomenon on an ink jet record form, and is different spreads and it is easy to reduce image quality greatly in case the liquid ink drop of two or more colors laps and is recorded, when especially ink rate of absorption is slow, it is required to give ink absorptivity high as an ink jet record form.

[0005] In order to solve these problems, very many techniques are proposed from the former.

[0006] As the pigment in the clad layer indicated by the ink jet record form which carried out humidity of the coating for surface treatment to the low size stencil indicated by JP,52-53012,A, the ink jet record form which prepared the coated layer of ink absorptivity in the support surface indicated by JP,55-5830,A, and JP,56-157,A The ink jet record form containing non-colloid silica powder, the ink jet record form which used together the inorganic pigment indicated by JP,57-107878,A and the organic pigment, The ink jet record form which has two hole distribution peaks indicated by JP,58-110287,A, The ink jet record form which consists of a vertical two-layer porous layer indicated by JP,62-111782,A, The ink jet record form which has the infinite form crack indicated by JP,59-68292,A, 59-123696, 60-18383, etc., The ink jet record form which has the impalpable powder layer indicated by JP,61-135786,A, 61-148092, 62-149475, etc., JP,63-252779,A, JP,1-108083,A, 2-136279, The ink jet record form containing the pigment which has the specific physical-properties value indicated by 3-65376, 3-27976, etc., or a particle silica, JP,57-14091,A, 60-219083, 60-210984, 61-20797, 61-188183, JP,5-51470,A, 5-278324, 6-92011, 6-183134, The ink jet record form containing particle silicas, such as a colloid silica indicated by 7-137431, 7-276789, etc., And JP,2-276671,A, 3-67684, 3-215082, Many ink jet record forms containing the hydrated alumina particle indicated by 3-251488, 4-67986, 4-263983, 5-16517, etc.. are known.

[0007] However, since many ink absorbing layers with many openings will have irregularity with micro interface with air and coat front face, the incident light to an ink absorbing layer is scattered about or transparency is barred when an ink absorbing layer absorbs ink or it consists of only layers which have many openings for holding, it becomes or tends to be hard to come out opaquely lusterless.

[0008] Moreover, in order to form an opening, there is a fault out of which the smooth nature on the front face of a coat by own irregularity of a pigment or the irregularity of the secondary floc of a pigment falls, and gloss cannot come easily.

[0009] Then, although the technique which gives high glossiness by carrying out calender processing of the gloss manifestation layer which turns into an ink acceptance layer from a colloidal particle with a mean particle diameter of 300nm or less represented by the amorphous silica alumina as a principal component at JP,7-101142,A in order to give gloss further after this one by one at a laminating and 7-117335 was indicated, by this approach, ink absorptivity and glossiness became scramble and were not able to say that it was enough.

[0010] Furthermore, it was difficult to obtain the high image of color repeatability or the depth of shade, an image becoming whitish, having the fault of color repeatability and the depth of shade falling, and maintaining high glossiness and transparency in an ink absorbing layer with many openings, since light stops easily being able to reach the ink which permeated the opening.

[0011]

[Problem(s) to be Solved by the Invention] This invention is made in view of the above-mentioned actual condition, and the object of this invention is in printing by water color ink to offer the ink jet record approach using the ink jet record form and this which have high ink absorptivity and made possible high-definition image formation with high glossiness and transparency.

[0012]

[Means for Solving the Problem] The above-mentioned object of this invention is attained by the following configurations.

[0013] 1. Ink-jet record form characterized by for mean particle diameter of solid-state particle (A) contained in opening layer of side separated from base material in ink jet record form which comes to prepare at least two-layer opening layer containing solid-state particle and hydrophilic binder on base material to be smaller than mean particle diameter of solid-state particle (B) contained in opening layer of side nearer than base material, and for the sum total of void volume of said opening layer to be two or more 20 ml/m.

[0014] 2. Ink jet record form given in said 1 characterized by said base material being hydrophobic base material.

[0015] 3. Said 1 to which said solid-state particle (A) is characterized by being silica system particle with a mean particle diameter of 7-30nm, or ink jet record form given in 2.

[0016] 4. Said 1 characterized by being calcium-carbonate particle said whose solid-state particle (A) is mean particle diameter of 10-50nm, or ink jet record form given in 2.

[0017] 5. Said 1 characterized by being alumina or hydrated alumina particle said whose solid-state particle (A) is mean particle diameter of 10-100nm, or ink jet record form given in 2.

[0018] 6. Ink jet record form given in said any 1 term of 1-5 to which said solid-state particle (B) is characterized by being silica system particle with a secondary [ an average of ] particle size of 1-10 micrometers.

[0019] 7. Ink jet record form given in said any 1 term of 1-6 characterized by at least one sort of said hydrophilic binder being polyvinyl alcohol or cation denaturation polyvinyl alcohol.

[0020] 8. Ink jet record approach characterized by printing on conditions from which amount of maximum regurgitation ink becomes said any 1 term of 1-7 with two or more 20 ml/m using ink jet recording ink which contains water soluble dye in ink jet record form of publication.

[0021] Hereafter, this invention is explained to a detail.

[0022] The opening layer which the ink jet record form of this invention has consists of the opening formed between solid-state particles the binder of a hydrophilic property, inorganic, or organic.

[0023] The formation approach of the typical opening by the solid-state particle is explained below.

[0024] (1) Apply the coating liquid containing a porosity solid-state particle and a hydrophilic binder

on a base material. The approach of forming an opening between the inside of a porosity particle, or a particle, the approach of applying the coating liquid containing the solid-state particle which has the volume more than equivalent weight (preferably 1.0 or more times) in general to (2) hydrophilic-property binder, and a hydrophilic binder on a base material, and creating an opening between solid-state particles, (3) Approach mean particle diameter makes solid-state particle about 0.1 micrometers or less condense at the time of coating liquid preparation or coat formation, forms a secondary particle or the three-dimensional structure, and creates an opening.

[0025] As for the opening formation approach in the ink jet record form of this invention, it is desirable to use the approach of not much not reducing the glossiness of an ink jet record form, by any aforementioned approach, although it is good. Although the approach (1) was generally excellent in ink absorptivity and it was widely used by coat paper etc. from before, the porosity solid-state particle was a particle with the big particle diameter of the micron order which the secondary most is condensing so that it might be represented by the synthetic infinite form silica, and was difficult to acquire glossiness sufficient in just the opening layer obtained by this approach.

[0026] In the condition of having not covered said swelling layer by making the swelling layer which consists of a hydrophilic binder forming in the maximum front face of the ink jet detail paper, even if the gloss of the opening layer itself is a low case somewhat, existence of a surface swelling layer can give high glossiness. However, when the size of the irregularity of an opening layer is too large, since the glossy high grant by the swelling layer is absorbed by the lower layer opening layer after it becomes difficult and is temporarily absorbed by this swelling layer, the rate of absorption of ink becomes rate-limiting [ the rate of absorption of the ink to a surface swelling layer ], and it becomes slow. The more it thickens this surface swelling layer for the reason on a surface gloss disposition, this inclination will become strong and, the more the absorptivity of ink will show only absorptivity comparable as the time of the whole being a swelling layer substantially.

[0027] Then, it found out that high glossiness could be given, maintaining high ink absorptivity by preparing the opening layer which contains a two-layer solid-state particle at least on a base material in this invention, and preparing the opening layer for which the mean particle diameter of the solid-state particle (A) contained in the layer of the side which is separated from a base material used the small particle compared with the mean particle diameter of the solid-state particle (B) contained in the layer of a near side from the base material.

[0028] Here, although the mean particle diameter of a solid-state particle (A) should be just small compared with it of a solid-state particle (B), it depends 1/5 preferably and is 1/10 preferably.

[0029] It is using the above (2) thru/or (3) for formation of the opening layer for ink absorption of the ink jet record form of this invention as a desirable approach as an opening layer of the side (upper layer) which is separated from a base material.

[0030] Moreover, when a swelling layer is prepared as the middle class between two-layer opening layers, as for ink rate of absorption, it is desirable that the layer which this medium swelling layer may become rate-limiting, may become late depending on a binder presentation or thickness, and contains said solid-state particle (A), and the layer containing said solid-state particle (B) adjoin.

[0031] When there is an ink absorption layer in the opening layer containing a solid-state particle, as a solid-state particle, a well-known solid-state particle inorganic [ various kinds of ] or organic can be conventionally used in an ink jet record form. As an example of the non-subtlety particle used, white inorganic pigments, such as precipitated calcium carbonate, whiting, a magnesium carbonate, a kaolin, clay, talc, a calcium sulfate, a barium sulfate, a titanium dioxide, a zinc oxide, zinc hydroxide, zinc sulfide, zinc carbonate, a hydrotalcite, aluminum silicate, the diatom earth, a calcium silicate, a magnesium silicate, synthetic amorphous silica, a gaseous-phase method silica, colloidal silica, an alumina, a colloidal alumina, pseudo-boehmite, an aluminum hydroxide, a lithopone, a zeolite, and a magnesium hydroxide etc. can be mentioned

[0032] On the other hand as an example of an organic particle, polystyrene, polyacrylic ester, polymethacrylic acid ester, polyacrylamides, polyethylene, polypropylene, a polyvinyl chloride, polyvinylidene chlorides or these copolymers, a urea-resin, or melamine resin is mentioned.

[0033] As for the solid-state particle (A) of the point of high concentration being attained, and a clear image being recorded and being able to manufacture by low cost to this invention, it is

desirable to use the solid-state particle chosen from a silica particle, a calcium carbonate, and a hydrated alumina particle.

[0034] The synthetic silica which could use various kinds of well-known silica system particles by the ink jet conventionally as a silica system particle preferably used for this invention, for example, was compounded by wet or the gaseous-phase method, colloidal silica, and the silica of the configuration of the porosity silica arbitration which a primary particle condenses and forms the secondary particle can be used. As such an example, for example, the synthetic amorphous silica indicated by JP,55-51583,A, 56-148583, etc., For example, the silica ultrafine particle compounded by the gaseous-phase method indicated by JP,60-204390,A, The synthetic infinite form silica containing the fluorine indicated by JP,60-222282,A; The synthetic infinite form silica in which surface treatment was carried out by the silane coupling agent indicated by JP,60-224580,A and 62-178384, For example, the spherical silica indicated by JP,62-183382,A and 63-104878, The synthetic silica particle whose Na<sub>2</sub>O content indicated by JP,63-317381,A is 0.5 % of the weight or more, The specific surface area indicated by JP,1-115677,A The synthetic silica particle more than 100m<sup>2</sup>/g, The synthetic silica particle which was indicated by JP,62-286787,A and by which alumina surface treatment was carried out, The synthetic silica particle by which surface treatment was carried out by calcium and Mg which were indicated by JP,1-259982,A, or Ba, The colloidal silica oil absorption was indicated to be by a 180ml [/g] or more composition silica particle and JP,57-14091,A, The cationic colloidal silica indicated by JP,60-219084,A, JP,6-92011,A, 6-297830, and 7-81214, And the colloidal silica which connected in the shape of [ which was indicated by JP,5-278324,A and 7-81214 ] a rosary, or branched can be mentioned.

[0035] However, in order to obtain high glossiness and high void volume, it is desirable to use the silica ultrafine particle whose mean particle diameter is 7-30nm for the opening layer of the side separated especially from the base material. This silica particle may be the object which cation denaturation could be carried out in the front face, and was processed by aluminum, calcium, Mg, Ba, etc.

[0036] moreover, as a calcium carbonate preferably used for the ink jet record form of this invention For example, JP,57-12486,A, 57-129778, 58-55283, The precipitated calcium carbonate which has specific surface area in the specification indicated by 61-20792, The needle pillar-shaped calcium carbonate indicated by JP,63-57277,A \*\*\*\* JP,4-250091,A, The calcium-carbonate particle which the specific needlelike primary particle indicated by JP,3-251487,A condensed, and formed the secondary particle, the needle which has the specific oil absorption indicated by JP,4-250091,A and 4-260092 — a pillar-shaped prismatic crystal Argo night calcium carbonate, the spherical precipitated calcium carbonate indicated by JP,7-40648,A are mentioned.

[0037] It is desirable that particle size uses calcium-carbonate particle about 0.1 micrometers or less for the opening layer of the side separated especially from the base material, and it is desirable to use the calcium-carbonate particle especially whose mean particle diameter is 10-50nm.

[0038] Furthermore, in the opening layer of the side separated from the base material, the mean particle diameter of an alumina or hydrated alumina has desirable about 0.2 micrometers or less, especially the alumina or hydrated alumina preferably used for this invention has the pore whose radius it is 10-100nm and is 3-10nm, and it is especially desirable that they are the porosity alumina whose sum of this pore volume is 0.2 – 2 ml/g, or its hydrated compound. The measurement means of pore volume can be measured with a well-known nitrogen adsorption process to an alumina or the desiccation solid content of hydrated alumina.

[0039] An alumina or hydrated alumina may be crystallinity, or may be amorphous, and although a configuration can use the object of the configuration of arbitration, such as an infinite form particle, a spherical particle, and a fiber particle, in order to obtain high void volume, it is desirable to use a fibrous thing.

[0040] Moreover, the solid-state particle (B) of this invention has the desirable silica particle points, such as ink absorptivity and low cost, to whose secondary [ an average of ] particle size is 1-10 micrometers.

[0041] The above-mentioned opening layer of the ink jet record form of this invention needs to contain the hydrophilic binder, in order to maintain the property as a coat.

[0042] However, it is important for a hydrophilic binder to swell, to swell in the activity of a hydrophilic binder, at the time of the osmosis in early stages of ink, and not to take up an opening substantially, and a hydrophilic binder with low bloating tendency is comparatively used preferably near a room temperature from this viewpoint. Especially a desirable hydrophilic binder is the polyvinyl alcohol or cation denaturation polyvinyl alcohol of perfect or partial saponification, and is \*\*.

[0043] one especially desirable also in polyvinyl alcohol — whenever [ saponification ] — 80 or more parts — or full saponification is carried out. Moreover, from a viewpoint which improves coat brittleness, 500—3500 are desirable especially desirable, and, as for the average degree of polymerization of polyvinyl alcohol, the thing of 1000—3500 is used.

[0044] Moreover, it is polyvinyl alcohol which has the 1—3rd class amino group which is indicated by JP,61—10483,A, for example, and the 4th class ammonium in the principal chain of the above-mentioned polyvinyl alcohol, or a side chain as cation denaturation polyvinyl alcohol.

[0045] Moreover, although other hydrophilic binders can be made to contain in said opening layer, as for those hydrophilic binders, it is preferably desirable that it is 20 or less % of the weight in general to the above-mentioned polyvinyl alcohol or cation denaturation polyvinyl alcohol.

[0046] Next, when forming the opening layer of the side which is separated from the opening layer of the ink jet record form of this invention, especially a base material, said approach (2) used preferably and (3) are further explained to a detail below.

[0047] It is good to carry out voidage preferably by said approach (2) more than 150 capacity %. Although the upper limit of voidage generally changes with the class of bulking agent, or the classes of hydrophilic binder, generally it is below 200 capacity % from the reinforcement as a coat, brittleness, etc.

[0048] Especially in order to carry out voidage to more than 100 capacity %, the ratio of a solid-state particle and a hydrophilic binder is important, and it is desirable that the weight ratio to the hydrophilic binder of this solid-state particle carries out to 10 or more and less than 200 by this approach. This weight ratio becomes difficult [ it / for void volume to obtain 100% or more less than by ten ], and the brittleness of a coat deteriorates in the case of 200 or more.

[0049] In this case, it is desirable to use a calcium—carbonate particle, an aforementioned alumina, or an aforementioned hydrated alumina particle especially.

[0050] Said approach (3) is the approach of forming a flocculation condition and forming the network structure into a coat, and into the water solution which contains a hydrophilic binder preferably, the primary ultrafine particle in a distributed condition is formed via the condition of condensing each other, where a point of contact is restricted comparatively. that such a flocculation condition is linear or the condition that what formed floc in the shape of branching was distributed in the water solution — or the condition of such flocs condensing each other further and taking the three-dimension network structure in a water solution is included.

[0051] Even if it is which case, detailed structure can be formed into the formed coat by carrying out spreading desiccation of this water solution on a base material.

[0052] Thus, in general, from the magnitude of a primary particle, the magnitude of the detailed opening in the obtained coat is about several times those magnitude of this, and has the description which is the opening of detailed magnitude.

[0053] It is formed in the water solution which has the approach of being hard to condense a primary particle to each other, carrying out ultralow—volume addition of the hydrophilic polymer which accelerates condensation of a particle in the water solution containing the hydrophilic polymer which can exist in stability as an approach of forming such a flocculation condition, for example, and forming condensation slightly, or the water—soluble polymer which can perform a primary particle front face and weak coupling.

[0054] It is desirable from that the latter approach tends to form the amount of an opening in stability especially in this invention that it is comparatively easy to control, that more amounts of openings are obtained as compared with the amount of the particle to be used, and a coat with the still higher glossiness of a coat being obtained.

[0055] In this case, especially a desirable thing is the case where use said particle silica as a primary particle, and polyvinyl alcohol or cation denaturation polyvinyl alcohol is used as a

hydrophilic binder. In this case, hydrogen bond with weak silanol group of a particle silica front face and hydroxyl group of vinyl alcohol is performed, and a flocculation object is formed.

[0056] The particle silica compounded by the synthetic approach called a gaseous-phase method especially as such a particle silica is used preferably.

[0057] By this approach, as a hydrophilic binder, as for especially the polymerization degree of the polyvinyl alcohol used preferably, 1000 or more are desirable, and it is desirable in order for 1500 especially or more to carry out for not causing a crack to a coat.

[0058] Here, the ratios of polyvinyl alcohol and the above-mentioned silica are 1:10-1:1 in general, and the range of them is 1:7-1:2 preferably.

[0059] It explains briefly [ below ] about the approach of forming the coat which contains a flocculation object using polyvinyl alcohol and a particle silica.

[0060] In the polyvinyl alcohol water solution (in general 5 - 15%) which maintained pH at 6-8, and the temperature of about 40 degrees C, it adds gradually, strong-agitating silica dispersion liquid (in general 5 - 15%), and an ultrasonic disperser, a high-speed homogenizer, etc. distribute after addition termination. In this case, various kinds of surfactants may be made to exist if needed. Subsequently, after adding various kinds of additives, it adjusts to target viscosity required for spreading, and the coat which has the above-mentioned opening by applying and drying by the well-known approach on a base material is obtained.

[0061] Although it is desirable in this invention to contain various kinds of oil droplets in order to improve the brittleness of a coat the solubility over water [ in / as such an oil droplet / a room temperature ] — about 0.01 or less % of the weight of a hydrophobic high-boiling point organic solvent (for example, a liquid paraffin —) dioctyl phthalate, tricresyl phosphate, a silicone oil, etc. and a polymer particle (for example, styrene —) The particle to which the polymerization of the one or more sorts was carried out for polymerization nature monomers, such as butyl acrylate, a divinylbenzene, butyl methacrylate, and hydroxyl ethyl methacrylate, can be made to contain. Such an oil droplet can be preferably used ten to 50% of the weight to a hydrophilic binder.

[0062] The sum total of the void volume of the opening layer of the ink jet record form of this invention is two or more [ 20ml //m / per two ] 1m of ink jet record forms. When the sum total of void volume is less than two 20 ml/m, although the absorptivity of the amount of low ink is good, ink overflows in the case of printing of the high amount of ink, image quality is reduced or problems, like drying [ after printing ] is late tend to generate it.

[0063] On the other hand, although especially the upper limit of the sum total of void volume is not restricted, the desiccation thickness of an opening layer is two or less 40 ml/m in general from it being required in order that making it 50 micrometers or less in general may not worsen the physical characteristic of coats, such as a crack.

[0064] Therefore, in order to attain the sum total of two or more 20 ml/m void volume, it is desirable to carry out voidage of an opening layer more than 100 capacity %.

[0065] Void volume is the value which deducted the total amount of the capacity of solid content, such as a binder in an opening layer, and various kinds of bulking agents, from the desiccation thickness in an opening layer, and voidage shows the rate of the amount of openings to the capacity of these solid content here.

[0066] It is the range which does not have an adverse effect on the effectiveness in this invention, and a bloating tendency ink absorption layer may be prepared. In this case, since it is required to show high bloating tendency to a liquid ink drop, the hydrophilic binder in which liquid ink bloating tendency is shown is used as a main configuration of this swelling layer. As a hydrophilic binder used preferably For example, gelatin or a gelatin derivative, a polyvinyl pyrrolidone (about 200,000 or more have desirable average molecular weight), A pullulan, polyvinyl alcohol or its derivative, a polyethylene glycol (100,000 or more have desirable average molecular weight), A carboxymethyl cellulose, hydroxyethyl cellulose, a dextran, A dextrin, polyacrylic acid and its salt, an agar, a kappa carrageenan, lambda-carrageenan, iota-carrageenan, xanthene gum, locust bean gum, A polyalkylene oxide system copolymerization nature polymer given in an alginic acid, gum arabic, a pullulan, JP,7-195826,A, and 7-9757, Polymers, such as independent or a copolymer which repeats and has these vinyl monomers of the vinyl monomer which has the carboxyl group and sulfonic group of a publication, can be mentioned to a water-soluble polyvinyl butyral or JP,62-245260,A.

These hydrophilic binders may be used independently and may use two or more sorts together. [0067] Since a swelling layer needs to have the early permeability and the bloating tendency over liquid ink, it contains at least one sort as which 200,000 or more polyvinyl pyrrolidones are chosen as for molecular weight, and about 50,000 or more polyethylene oxide and molecular weight are chosen for molecular weight from the copolymer of 100,000 or more polyethylene oxide and polypropylene oxide, hydroxyethyl cellulose, and polyacrylamide preferably as a hydrophilic binder of a swelling layer.

[0068] Moreover, it is desirable to use reversibly a part of hydrophilic binder in which sol gel transformation is possible from a viewpoint of stability high-speed spreading, and it is desirable from this point to use at least one sort of gelatin, a gelatin derivative, and a kappa carrageenan.

[0069] In this invention, various kinds of well-known surfactants can be used. In order to make the flare degree of a liquid ink drop large comparatively, it is desirable to use the surfactant which generally lowers surface tension, and it is desirable to use an anion system surfactant and a fluorocanthical surfactant especially.

[0070] Various kinds of additives can be made to contain if needed in the ink receptiveness layer of the arbitration of the ink jet record form of this invention.

[0071] For example, an ultraviolet ray absorbent given in JP,57-74193,A, 57-87988, and 62-261476, JP,57-74192,A, 57-87989, 60-72785, The fading inhibitor indicated by 61-146591, JP,1-95091,A, 3-13376, etc., An anion, a cation or the various surfactants of Nonion, JP,59-42993,A, The fluorescent brightener indicated by 59-52689, 62-280069, 61-242871, JP,4-219266,A, etc., Various well-known additives, such as lubricant, such as pH regulators, such as a sulfuric acid, a phosphoric acid, a citric acid, a sodium hydroxide, a potassium hydroxide, and potassium carbonate, a defoaming agent, and a JIECHIREN glycol, antiseptics, a thickener, a hardening agent, an antistatic agent, and a mat agent, can also be made to contain.

[0072] An inorganic or organic hardening agent can be used as a hardening agent, for example, chromium alum, formaldehyde, a glyoxal, an epoxy system compound, a vinyl sulfone system compound, an acryloyl system compound, s-triazine system compound, N-methylol system compound, a carbodiimide system compound, ethylene imino \*\*\*\*\* etc. can be used.

[0073] Into the configuration layer of the arbitration by the side of the ink recording surface of this invention, an alkali-metal weak acid salt the poly allylamine of publications, such as the poly cation polyelectrolyte of JP,56-84992,A, a basic latex polymer of JP,57-36692,A, JP,4-15744,B, JP,61-58788,A, and 62-174184, and given in JP,61-47290,A etc. can be used more than a kind as a deck-watertight-luminaire-ized agent of an image.

[0074] As a base material of the ink jet record form of this invention, a thing well-known as a record form for ink jets can be used suitably conventionally.

[0075] The thing of a property which bears the radiant heat when being able to mention the film which consists of ingredients, such as polyester system resin, diacetate system resin, triacetate system resin, acrylic resin, polycarbonate system resin, polyvinyl chloride system resin, polyimide system resin, cellophane, and celluloid, a plate, a glass plate, etc. as a transparence base material, for example, and being used as an OHP also in this is desirable, and especially polyethylene terephthalate is desirable. As thickness of such a transparent base material, about 10-200 micrometers is desirable.

[0076] Moreover, although what carried out opacification processing of the sheet which consists of common paper, a synthetic paper, resin coat paper, cloth, timber, a metal, etc. as a base material to be used, for example, a plate, and the above-mentioned translucency base material with the well-known means can be mentioned when there is no transparent need The so-called White pet which comes to add white pigments to the resin coat paper (the so-called RC paper) which has the polyolefin resin enveloping layer which added white pigments etc. at least to one side of a base paper, and polyethylene terephthalate is desirable. It is desirable to perform corona discharge treatment, undercoating processing, etc. to a base material in advance of spreading of an ink absorbing layer for the object, such as to enlarge bond strength of a base material and an ink television layer. Furthermore, the ink jet record form of this invention does not necessarily need to be colorlessness, and may be a colored ink jet record form.

[0077] Also in these, as a base material of this invention, a hydrophobic base material is desirable,

for example, are polyethylene terephthalate, polyolefin resin coat paper, and the White pet.

[0078] Although it can carry out by choosing suitably the approach of applying the layer containing the non-subtlety particle of this invention on a base material from a well-known approach, the extrusion coat method which uses a hopper the roll coat method, the rod bar coat method, the air knife coat method, a spray coating method, the curtain coat method, or given in a U.S. Pat. No. 2681294 official report is used preferably.

[0079] Moreover, after it cools and the gel state takes after applying on a base material as indicated by JP,6-64306,A in using the hydrophilic binder in which sol gel transformation, such as gelatin, and a gelatin derivative, a kappa carrageenan, is possible, you may carry out by the approach of drying by the cold dry cleaning method.

[0080] In case image recording is carried out using the ink jet record form of this invention, the record approach which used water color ink is used.

[0081] The ink jet recording ink (only henceforth ink jet recording ink) containing the water soluble dye said by this invention is the following water soluble dye and a solvent object, and recording ink that consists of other additives. Water soluble dye, such as direct dye well-known as water soluble dye at an ink jet, acid dye, basic dye, reactive dye, or a food dye, can be used.

[0082] As a solvent of ink jet recording ink, water and water-soluble, various organic solvents, For example, methyl alcohol, isopropyl alcohol, n-butyl alcohol, Alcohols, such as tert-butyl alcohol and isobutyl alcohol; Dimethylformamide, Amides, such as dimethylacetamide; Ketones, such as an acetone and diacetone alcohol, or a ketone-alcohol; tetrahydrofuran, Ether, such as dioxane; Polyalkylene glycols; ethylene glycol, such as a polyethylene glycol and a polypropylene glycol, Propylene glycol, a butylene glycol, triethylene glycol, 1, 2, 6-hexane triol, thiodiglycol, hexylene glycol, Polyhydric alcohol, such as a diethylene glycol, a glycerol, and triethanolamine; Ethylene glycol methyl ether, The low-grade alkyl ether of polyhydric alcohol, such as the diethylene-glycol methyl (or ethyl) ether and the triethylene glycol monobutyl ether, is mentioned.

[0083] Also in the water-soluble organic solvent of these many, the low-grade alkyl ether of the polyhydric alcohol of polyhydric alcohol, such as a diethylene glycol, triethanolamine, and a glycerol, and the triethylene glycol monobutyl ether etc. is desirable.

[0084] As an additive of other ink jet recording ink, pH modifier, a sequestering agent, an antifungal agent, a viscosity controlling agent, a surface tension regulator, a wetting agent, a surfactant, a rusr-proofer, etc. are mentioned, for example.

[0085] In order that the wettability to an ink jet record form may make it good, in 20 degrees C, ink jet recording ink has desirable 25 – 60 dyn/cm, and it is desirable to have the surface tension of 30 – 50 dyn/cm within the limits more preferably.

[0086] the ink jet recording method in which the regurgitation [ ink jet recording ink ] of the ink regurgitation method at the time of carrying out image recording using the ink jet record form of this invention is possible — it is — \*\*\*ing — for example, "ink jet record technical trend" Nakamura [ Koichi ] editing — recording methods, such as a continuation injection electrification control system, a method on demand, etc. of a publication, can be used for work (Japanese Science-information, 1995) p.1-14. However, bigger effectiveness can be acquired by using it also in these, applying to the recording method of a method on demand.

[0087] The ink maximum delivery in this invention is the maximum of the amount of ink volume per [ which can be used when the ink jet printer used for this invention outputs all the usual images ] unit volume. For example, it is not necessarily the ink maximum delivery which added the amount of ink for obtaining the maximum density of yellow, Magenta, cyanogen, and black each monochrome in the case of the printer for color pictures. An ink maximum delivery can be calculated by count, if the volume of one drop of ink jet recording ink is known and the array approach of the drop for forming an image is known.

[0088]

[Example] Although the example of this invention is given and explained below, this invention is not limited to these examples. In addition, in an example, especially, as long as there is no notice, oven-dry-weight % is shown "%."

[0089] To the recording surface side on the paper base material (in the polyethylene layer by the side of 140 micrometers in thickness, and a recording surface, anatase mold titanium-dioxide

content is carried out, and it has 7% of the weight of the layer which contains alkali treatment gelatin 1.2 g/m<sup>2</sup> and a hardening agent as a back layer in the rear-face side of a recording surface) which covered 1100g of examples/, and stencil both sides of m<sup>2</sup> with polyethylene, it applied and the following [coating liquid -1] was dried so that humid thickness might turn to 125 micrometers. [0090]

[Coating liquid -1]

Pure water 980ml Particle silica with a mean particle diameter of about 2.5 micrometers 48.2g Polyvinyl alcohol of average degree of polymerization 1700 (whenever [ saponification ] 90%) 24.1g Surfactant -1 1.2g [0091]

[Formula 1]

界面活性剤-1



[0092] Subsequently, the coating liquid -2 of the following presentations was applied by 100 micrometers of humid thickness on this spreading layer, it dried, and the ink jet record form -1 of this invention was obtained. Thus, the sum total of the void volume of the obtained coat was 24 ml/m<sup>2</sup>.

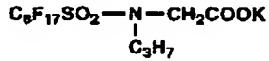
[0093]

[Coating liquid -2]

Pure water 980ml Particle silica with a mean particle diameter of about 7nm 48.2g Polyvinyl alcohol of average degree of polymerization 3500 (whenever [ saponification ] 90%) 16.1g Surfactant -2 1.2g [0094]

[Formula 2]

界面活性剤-2



[0095] Next, ink jet record form which changed coating liquid as follows respectively using [ on the ink jet record form -1 and ] [coating liquid -1] and [coating liquid -2] - 2-10 were created like the ink jet record form -1.

[0096] Ink jet record form - It is the same as the ink jet record form -1 except having not applied 2: [coating liquid -2], but [coating liquid -1] having performed spreading twice by 125 micrometers of humid thickness. (The sum total of void volume = about 25 ml/m<sup>2</sup>)

Ink jet record form - It is the same as the ink jet record form -1 except having applied the humid thickness of 3: [coating liquid -1] by 140 micrometers of humid thickness of 80 micrometers and [coating liquid -2]. (The sum total of void volume = about 24 ml/m<sup>2</sup>)

Ink jet record form - It is the same as the ink jet record form -1 except having used the silica with a mean particle diameter of 1.4 micrometers instead of the silica with a mean particle diameter [ of 4: [coating liquid -1] ] of 2.5 micrometers. (The sum total of void volume = about 23 ml/m<sup>2</sup>)

Ink jet record form - It is the same as the ink jet record form -1 except having used the colloid silica with a mean particle diameter of 0.1 micrometers instead of the silica with a mean particle diameter [ of 5: [coating liquid -1] ] of 2.5 micrometers. (The sum total of void volume = about 21 ml/m<sup>2</sup>)

Ink jet record form - After changing the surfactant of 2 and [coating liquid -2] into 1 for the surfactant of 6: [coating liquid -1] and applying [coating liquid -2], it is the same as the ink jet record form -1 except having applied [coating liquid -1]. (The sum total of void volume = about 24 ml/m<sup>2</sup>)

Ink jet record form - It is the same as the ink jet record form -1 except having performed each humid thickness of 7: [coating liquid -1] and [coating liquid -2] by 80 micrometers. (The sum total of void volume = about 16 ml/m<sup>2</sup>)

Ink jet record form - The mean particle diameter of 8 micrometers is the same as the ink jet

record form -1 instead of a particle silica with a mean particle diameter [ of 8: [coating liquid -1] ] of 2.5 micrometers except having used the particle silica. (The sum total of void volume = about 23 ml/m<sup>2</sup>)

Ink jet record form - The mean particle diameter of 12 micrometers is the same as the ink jet record form -1 instead of a particle silica with a mean particle diameter [ of 9: [coating liquid -1] ] of 2.5 micrometers except having used the particle silica. (The sum total of void volume = about 24 ml/m<sup>2</sup>)

Ink jet record form - The mean particle diameter of 7nm of 10: [coating liquid -2] is the same as the ink jet record form -1 except having used the colloid child silica with a mean particle diameter of 50nm instead of the particle silica. (The sum total of void volume = about 23 ml/m<sup>2</sup>)

About each obtained ink jet record form, using ink jet printer MJ[ by Seiko Epson, Inc. ]-5100C, the assessment pattern was printed and the following items were evaluated.

[0097] (1) Ink absorption capacity : when 30% of the amount of the maximum ink of \*\* yellow, 60% of regurgitation of the amount of the maximum ink of each ink of cyanogen, and Magenta ink was made to breathe out at the time of 60% of regurgitation of the amount of the maximum ink of each ink of \*\* yellow and cyanogen, the condition of the overflow of the ink in each case was observed visually.

[0098] [The overflow of ink]

O x dried within about 10 seconds although it is overflowing slightly immediately after \*\*:printing which does not overflow at all immediately after :printing : it takes a front face 10 seconds or more to overflow immediately after printing and to dry.

[0099] (2) Ink absorptivity : homogeneity was made to breathe out and it recorded so that it might become 30% of the amount of the maximum ink, respectively, and 20 red-reflex concentration of the solid section was measured using the microdensitometer (aperture =200micrometerphi), and the value of \*\* yellow and cyanogen broken by average reflection density in quest of the standard deviation of the variation in the concentration was calculated. When ink absorptivity is good, the value of non-Lycium chinense becomes [ nonuniformity ] small at an image, but if ink absorptivity falls, this each other liquid ink drops will cause beading mutually in the ink jet record paper, it will become nonuniformity, and this value will increase.

[0100] (3) Drying : time amount until it leaves a regular paper in piles and ink stops imprinting 60% printing section of yellow and a Magenta in a regular paper after after [ printing ] fixed time amount progress was found.

[0101] (4) Dot diameter : the single dot of black was printed in the single dot diameter (K) of black ink, and the yellow solid printing section, and they were observed and asked for the diameter under the microscope (K/Y). The diameter measured the area of 20 dots, respectively and asked for this as the average of the diameter when carrying out circle conversion. (Unit: micrometer)

(5) Glossiness : gloss was measured for the printing side 75 degrees using the deflection glossmeter (VGS-1001DP) by Nippon Denshoku Industries Co., Ltd.

[0102] The obtained result is shown in a table 1.

[0103] <BR> [A table 1]

記録用紙	インクジェット		インク吸収量	インク吸収性	乾燥性	ドット直径		光沢度 (%)
	①	②				K	K/Y	
1 (本発明)	○	○	0.09	2分	80	110	66	
2 (比較例)	○	○	0.06	1分	100	150	5	
3 (本発明)	○	○	0.10	2分	80	110	67	
4 (本発明)	○	○	0.10	2分	90	110	70	
5 (比較例)	○	△	0.13	3分	90	130	72	
6 (比較例)	○	○	0.07	1分	100	140	8	
7 (比較例)	△	×	0.18	4分	60	(a)	68	
8 (本発明)	○	△	0.09	2分	80	110	60	
9 (本発明)	○	○	0.09	2分	80	110	51	
10 (本発明)	○	○	0.11	2分	90	110	68	

(a) 測定不能

[0104] Ink jet record form of the result of a table 1 to this invention - It turns out that 1, 3, 4, and 8 have a high ink absorption capacity, good ink absorptivity, and glossiness high in a drying list, and

dot size is small suitable for high definition ink jet record. On the other hand, although ink absorptivity and drying are good, glossiness falls substantially, and even if dot size is large and moreover micrifies a liquid ink drop, a high-definition image can obtain easily neither the ink jet record form -6 which used the big particle of a mean diameter for the side separated from the base material, nor the ink jet record form -2 only using the big particle of a mean diameter.

[0105] As for the ink jet record form -5 using the small particle of the mean diameter of the particle of a side far from a base material, lowering of ink absorptivity is seen at the side near a base material. The sum total of void volume is small, ink absorption capacity was lacking and the high-definition image was not obtained for the ink jet record form -7.

[0106] Moreover, ink jet record form of this invention using the big particle of a larger mean diameter than the particle contained in the ink jet record form which is the desirable mode of this invention - 9 and 10 are compared with the ink jet record form which is the desirable mode of this invention, and its glossiness is low a little.

[0107] It is an ink jet record form like an example 1 except having changed [coating liquid -2] into the following [coating liquid-2a] in example 2 example 1. - It is the ink jet record form of a configuration like 1-7. - 21-27 were created and it evaluated like the example 1.

[0108]

[Coating liquid-2a]

Pure water 960ml Particle calcium carbonate (mean particle diameter = about 0.03 micrometers) 76.9g Polyvinyl alcohol of average degree of polymerization 1700 (whenever [ saponification ] 90%) 9.6g Surfactant -1 1.2g of ink jet record forms -28 as well as the ink jet record form -21 was created again except having used the particle calcium carbonate with a mean particle diameter of 0.07 micrometers instead of the particle calcium carbonate with a mean particle diameter [ of [coating liquid-2a] ] of 0.03 micrometers.

[0109] The object for openings and swelling layer membrane thickness of each ink jet record form were as follows.

[0110] Ink jet record form - 21: sum total [ of void volume ] = — about 26 ml/m<sup>2</sup> ink-jet record form-22: — sum total [ of void volume ] = — about 25ml/m<sup>2</sup> 2 ink-jet record form-23: — sum total [ of void volume ] = — about 25 ml/m<sup>2</sup> ink-jet record form-24: — sum total [ of void volume ] = — about 25ml /m<sup>2</sup> ink-jet record form - 25: sum total [ of void volume ] = — about 23 ml/m<sup>2</sup> ink-jet record form-26: — sum total [ of void volume ] = — about 26 ml/m<sup>2</sup> ink-jet record form-27 : sum total [ of void volume ] = — about 19 ml/m<sup>2</sup> ink-jet record form-28: — sum total [ of void volume ] = — the ink jet record form of about 25 ml/m<sup>2</sup> \*\* The same assessment as an example 1 is performed, and a result is shown in a table 2.

[0111]

[A table 2]

インクジェット 記録用紙	インク吸収容量		インク吸収性	乾燥性	ドット直径		光沢度 (%)
	①	②			K	K/Y	
21 (本発明)	○	○	0.11	2分	90	110	68
22 (比較例)	○	○	0.06	1分	100	150	5
23 (本発明)	○	○	0.12	2分	90	110	72
24 (本発明)	○	○	0.12	2分	90	110	71
25 (比較例)	○	△	0.14	3分	90	120	74
26 (比較例)	○	○	0.07	1分	100	140	9
27 (比較例)	○	△	0.19	4分	60	(a)	68
28 (本発明)	○	○	0.13	3分	90	120	61

(a) 測定不能

[0112] Even if it changes to a particle silica and transposes to a particle calcium carbonate as an inorganic bulking agent from the result of a table 2, it turns out that the same effectiveness as an example 1 is acquired.

[0113] It is an ink jet record form like an example 1 except having changed [coating liquid -2] into the following [coating liquid-2bs] in example 3 example 1. - It is the ink jet record form of a configuration like 1-7. - 31-37 were created and it evaluated like the example 1.

[0114]

[Coating liquid-2b]

Pure water 200ml Alumina sol (catalyst formation the product made from Industry, Cataloid AS-3) 750ml Polyvinyl alcohol of average degree of polymerization 1700 (whenever [ saponification ] 90%) 7.6g Surfactant -1 Except having used the alumina of 1 micrometer of mean diameters instead of the alumina sol of [coating liquid-2b], the ink jet record form -38 as well as the ink jet record form -31 was created, and 1.2g was evaluated like the example 1 again.

[0115] The object for openings and swelling layer membrane thickness of each ink jet record form were as follows.

[0116] Ink jet record form - 31: sum total [ of void volume ] = — about 22 ml/m<sup>2</sup> ink-jet record form-32: — sum total [ of void volume ] = — about 25 ml/m<sup>2</sup> ink-jet record form-33: — sum total [ of void volume ] = — about 22 ml/m<sup>2</sup> ink-jet record form-34: — sum total [ of void volume ] = — an about 21 ml/m<sup>2</sup> ink-jet record form - 35: — sum total [ of void volume ] = — about 21ml [ /m ] 2 ink-jet record form-36: — sum total [ of void volume ] = — about 24 ml/m<sup>2</sup> ink-jet record form-37: — sum total [ of void volume ] = — about 15 ml/m<sup>2</sup> ink-jet record form-38: — sum total [ of void volume ] = — about 21 ml/m<sup>2</sup> result It is shown in a table 3.

[0117]

[A table 3]

インクジェット 記録用紙	インク吸収容量		インク吸収性	乾燥性	ドット直徑		光沢度 (%)
	①	②			K	K/Y	
31 (本発明)	○	○	0.11	2分	70	100	70
32 (比較例)	○	○	0.06	1分	100	150	5
33 (本発明)	○	○	0.12	2分	70	100	71
34 (本発明)	○	○	0.10	2分	70	100	72
35 (比較例)	○	△	0.11	3分	70	100	73
36 (比較例)	○	○	0.07	1分	90	130	8
37 (比較例)	△	×	0.21	5分	80	(a)	71
38 (本発明)	○	○	0.13	3分	80	140	62

(a) 測定不能

[0118] Even if it changes to a particle silica and transposes to particle alumina sol as an inorganic bulking agent from the result of a table 3, it turns out that the same effectiveness as an example 1 is acquired.

[0119] Although it was opaque and the case where a glossy paper base material was used was explained by this example, the suitable ink jet record form for the application using transparency of CFM used for color displays, such as the color-separation version at the time of creating what observes a record image by projection to a screen etc., and the positive version of color printing by optical instruments, such as a slide and OHP, or liquid crystal, can be offered by using a transparent base material.

[0120] Moreover, although the case where it mainly uses for an ink jet method has been explained about the ink jet record form of this invention, it can use suitable for record by record devices, such as various writing materials, a pen plotter, etc. which use water color ink besides an ink jet method.

[0121]

[Effect of the Invention] If the ink jet record approach using the configuration of the ink jet record form of this invention and this is used as the example proved, since the flare of the dot size in the record paper can be controlled small, maintaining high ink absorptivity even if it could attain good ink absorptivity and the liquid ink drop moreover micrified, maintaining high glossiness, a high-definition color picture is recordable.

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**TECHNICAL FIELD**

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**[Field of the Invention]** This invention relates to the ink jet record approach using the ink jet record form and this which were excellent in ink absorptivity and glossiness in more detail about the ink jet record approach using the ink jet record form and this which record using water color ink.

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PRIOR ART

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[Description of the Prior Art] although ink jet record makes the minute drop of ink fly by various working principles, and is made to adhere to record sheets, such as paper, and an image, an alphabetic character, etc. are recorded, a high speed, the low noise, and multiple-color-izing are comparatively easy — etc. — it has the advantage. About the blinding of a nozzle and the maintenance which had become a problem from the former by this method, from both sides of ink and equipment, amelioration progresses and it has spread through various fields, such as various printers, facsimile, and a computer terminal, quickly in current.

[0003] As an ink jet record form used by this ink jet recording method, also when a printing dot laps [ that a color tone is brightly skillful and absorption of ink ] early, the diffusion to the longitudinal direction of ink flowing out or not spreading and a printing dot is not large [ the concentration of a printing dot is high, and ] beyond the need, and it is required that the circumference should be smooth and should not fade etc.

[0004] Since it becomes nonuniformity, and the color of each other in the border area of a color which a drop causes a HAJIKI phenomenon on an ink jet record form, and is different spreads and it is easy to reduce image quality greatly in case the liquid ink drop of two or more colors laps and is recorded, when especially ink rate of absorption is slow, it is required to give ink absorptivity high as an ink jet record form.

[0005] In order to solve these problems, very many techniques are proposed from the former.

[0006] As the pigment in the clad layer indicated by the ink jet record form which carried out humidity of the coating for surface treatment to the low size stencil indicated by JP,52-53012,A, the ink jet record form which prepared the coated layer of ink absorptivity in the support surface indicated by JP,55-5830,A, and JP,56-157,A The ink jet record form containing non-colloid silica powder, the ink jet record form which used together the inorganic pigment indicated by JP,57-107878,A and the organic pigment, The ink jet record form which has two hole distribution peaks indicated by JP,58-110287,A, The ink jet record form which consists of a vertical two-layer porous layer indicated by JP,62-111782,A, The ink jet record form which has the infinite form crack indicated by JP,59-68292,A, 59-123696, 60-18383, etc., The ink jet record form which has the impalpable powder layer indicated by JP,61-135786,A, 61-148092, 62-149475, etc., JP,63-252779,A, JP,1-108083,A, 2-136279, The ink jet record form containing the pigment which has the specific physical-properties value indicated by 3-65376, 3-27976, etc., or a particle silica, JP,57-14091,A, 60-219083, 60-210984, 61-20797, 61-188183, JP,5-51470,A, 5-278324, 6-92011, 6-183134, The ink jet record form containing particle silicas, such as a colloid silica indicated by 7-137431, 7-276789, etc., And JP,2-276671,A, 3-67684, 3-215082, Many ink jet record forms containing the hydrated alumina particle indicated by 3-251488, 4-67986, 4-263983, 5-16517, etc. are known.

[0007] However, since many ink absorbing layers with many openings will have irregularity with micro interface with air and coat front face, the incident light to an ink absorbing layer is scattered about or transparency is barred when an ink absorbing layer absorbs ink or it consists of only layers which have many openings for holding, it becomes or tends to be hard to come out opaquely lusterless.

[0008] Moreover, in order to form an opening, there is a fault out of which the smooth nature on

the front face of a coat by own irregularity of a pigment or the irregularity of the secondary floc of a pigment falls, and gloss cannot come easily.

[0009] Then, although the technique which gives high glossiness by carrying out calender processing of the gloss manifestation layer which turns into an ink acceptance layer from a colloidal particle with a mean particle diameter of 300nm or less represented by the amorphism silica alumina as a principal component at JP,7-101142,A in order to give gloss further after this one by one at a laminating and 7-117335 was indicated, by this approach, ink absorptivity and glossiness became scramble and were not able to say that it was enough.

[0010] Furthermore, it was difficult to obtain the high image of color repeatability or the depth of shade, an image becoming whitish, having the fault of color repeatability and the depth of shade falling, and maintaining high glossiness and transparency in an ink absorbing layer with many openings, since light stops easily being able to reach the ink which permeated the opening.

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**EFFECT OF THE INVENTION**

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[Effect of the Invention] If the ink jet record approach using the configuration of the ink jet record form of this invention and this is used as the example proved, since the flare of the dot size in the record paper can be controlled small, maintaining high ink absorptivity even if it could attain good ink absorptivity and the liquid ink drop moreover micrified, maintaining high glossiness, a high-definition color picture is recordable.

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**TECHNICAL PROBLEM**

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**[Problem(s) to be Solved by the Invention]** This invention is made in view of the above-mentioned actual condition, and the object of this invention is in printing by water color ink to offer the ink jet record approach using the ink jet record form and this which have high ink absorptivity and made possible high-definition image formation with high glossiness and transparency.

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## MEANS

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[Means for Solving the Problem] The above-mentioned object of this invention is attained by the following configurations.

[0013] 1. Ink-jet record form characterized by for mean particle diameter of solid-state particle (A) contained in opening layer of side separated from base material in ink jet record form which comes to prepare at least two-layer opening layer containing solid-state particle and hydrophilic binder on base material to be smaller than mean particle diameter of solid-state particle (B) contained in opening layer of side nearer than base material, and for the sum total of void volume of said opening layer to be two or more 20 ml/m.

[0014] 2. Ink jet record form given in said 1 characterized by said base material being hydrophobic base material.

[0015] 3. Said 1 to which said solid-state particle (A) is characterized by being silica system particle with a mean particle diameter of 7–30nm, or ink jet record form given in 2.

[0016] 4. Said 1 characterized by being calcium–carbonate particle said whose solid-state particle (A) is mean particle diameter of 10–50nm, or ink jet record form given in 2.

[0017] 5. Said 1 characterized by being alumina or hydrated alumina particle said whose solid-state particle (A) is mean particle diameter of 10–100nm, or ink jet record form given in 2.

[0018] 6. Ink jet record form given in said any 1 term of 1–5 to which said solid-state particle (B) is characterized by being silica system particle with a secondary [ an average of ] particle size of 1–10 micrometers.

[0019] 7. Ink jet record form given in said any 1 term of 1–6 characterized by at least one sort of said hydrophilic binder being polyvinyl alcohol or cation denaturation polyvinyl alcohol.

[0020] 8. Ink jet record approach characterized by printing on conditions from which amount of maximum regurgitation ink becomes said any 1 term of 1–7 with two or more 20 ml/m using ink jet recording ink which contains water soluble dye in ink jet record form of publication.

[0021] Hereafter, this invention is explained to a detail.

[0022] The opening layer which the ink jet record form of this invention has consists of the opening formed between solid-state particles the binder of a hydrophilic property, inorganic, or organic.

[0023] The formation approach of the typical opening by the solid-state particle is explained below.

[0024] (1) Apply the coating liquid containing a porosity solid-state particle and a hydrophilic binder on a base material. The approach of forming an opening between the inside of a porosity particle, or a particle, the approach of applying the coating liquid containing the solid-state particle which has the volume more than equivalent weight (preferably 1.0 or more times) in general to (2) hydrophilic–property binder, and a hydrophilic binder on a base material, and creating an opening between solid-state particles, (3) Approach mean particle diameter makes solid-state particle about 0.1 micrometers or less condense at the time of coating liquid preparation or coat formation, forms a secondary particle or the three-dimensional structure, and creates an opening.

[0025] As for the opening formation approach in the ink jet record form of this invention, it is desirable to use the approach of not much not reducing the glossiness of an ink jet record form, by any aforementioned approach, although it is good. Although the approach (1) was generally excellent in ink absorptivity and it was widely used by coat paper etc. from before, the porosity

solid-state particle was a particle with the big particle diameter of the micron order which the secondary most is condensing so that it might be represented by the synthetic infinite form silica, and was difficult to acquire glossiness sufficient in just the opening layer obtained by this approach.

[0026] In the condition of having not covered said swelling layer by making the swelling layer which consists of a hydrophilic binder forming in the maximum front face of the ink jet detail paper, even if the gloss of the opening layer itself is a low case somewhat, existence of a surface swelling layer can give high glossiness. However, when the size of the irregularity of an opening layer is too large, since the glossy high grant by the swelling layer is absorbed by the lower layer opening layer after it becomes difficult and is temporarily absorbed by this swelling layer, the rate of absorption of ink becomes rate-limiting [ the rate of absorption of the ink to a surface swelling layer ], and it becomes slow. The more it thickens this surface swelling layer for the reason on a surface gloss disposition, this inclination will become strong and, the more the absorptivity of ink will show only absorptivity comparable as the time of the whole being a swelling layer substantially.

[0027] Then, it found out that high glossiness could be given, maintaining high ink absorptivity by preparing the opening layer which contains a two-layer solid-state particle at least on a base material in this invention, and preparing the opening layer for which the mean particle diameter of the solid-state particle (A) contained in the layer of the side which is separated from a base material used the small particle compared with the mean particle diameter of the solid-state particle (B) contained in the layer of a near side from the base material.

[0028] Here, although the mean particle diameter of a solid-state particle (A) should be just small compared with it of a solid-state particle (B), it depends 1/5 preferably and is 1/10 preferably.

[0029] It is using the above (2) thru/or (3) for formation of the opening layer for ink absorption of the ink jet record form of this invention as a desirable approach as an opening layer of the side (upper layer) which is separated from a base material.

[0030] Moreover, when a swelling layer is prepared as the middle class between two-layer opening layers, as for ink rate of absorption, it is desirable that the layer which this medium swelling layer may become rate-limiting, may become late depending on a binder presentation or thickness, and contains said solid-state particle (A), and the layer containing said solid-state particle (B) adjoin.

[0031] When there is an ink absorption layer in the opening layer containing a solid-state particle, as a solid-state particle, a well-known solid-state particle inorganic [ various kinds of ] or organic can be conventionally used in an ink jet record form. As an example of the non-subtlety particle used, white inorganic pigments, such as precipitated calcium carbonate, whiting, a magnesium carbonate, a kaolin, clay, talc, a calcium sulfate, a barium sulfate, a titanium dioxide, a zinc oxide, zinc hydroxide, zinc sulfide, zinc carbonate, a hydrotalcite, aluminum silicate, the diatom earth, a calcium silicate, a magnesium silicate, synthetic amorphous silica, a gaseous-phase method silica, colloidal silica, an alumina, a colloidal alumina, pseudo-boehmite, an aluminum hydroxide, a lithopone, a zeolite, and a magnesium hydroxide etc. can be mentioned

[0032] On the other hand as an example of an organic particle, polystyrene, polyacrylic ester, polymethacrylic acid ester, polyacrylamides, polyethylene, polypropylene, a polyvinyl chloride, polyvinylidene chlorides or these copolymers, a urea-resin, or melamine resin is mentioned.

[0033] As for the solid-state particle (A) of the point of high concentration being attained, and a clear image being recorded and being able to manufacture by low cost to this invention, it is desirable to use the solid-state particle chosen from a silica particle, a calcium carbonate, and a hydrated alumina particle.

[0034] The synthetic silica which could use various kinds of well-known silica system particles by the ink jet conventionally as a silica system particle preferably used for this invention, for example, was compounded by wet or the gaseous-phase method, colloidal silica, and the silica of the configuration of the porosity silica arbitration which a primary particle condenses and forms the secondary particle can be used. As such an example, for example, the synthetic amorphous silica indicated by JP,55-51583,A, 56-148583, etc., For example, the silica ultrafine particle compounded by the gaseous-phase method indicated by JP,60-204390,A, The synthetic infinite form silica containing the fluorine indicated by JP,60-222282,A, The synthetic infinite form silica in which surface treatment was carried out by the silane coupling agent indicated by JP,60-224580,A and

62-178384, For example, the spherical silica indicated by JP,62-183382,A and 63-104878, The synthetic silica particle whose Na<sub>2</sub>O content indicated by JP,63-317381,A is 0.5 % of the weight or more, The specific surface area indicated by JP,1-115677,A The synthetic silica particle more than 100m<sup>2</sup>/g, The synthetic silica particle which was indicated by JP,62-286787,A and by which alumina surface treatment was carried out, The synthetic silica particle by which surface treatment was carried out by calcium and Mg which were indicated by JP,1-259982,A, or Ba, The colloidal silica oil absorption was indicated to be by a 180ml [/g ] or more composition silica particle and JP,57-14091,A, The cationic colloidal silica indicated by JP,60-219084,A, JP,6-92011,A, 6-297830, and 7-81214, And the colloidal silica which connected in the shape of [ which was indicated by JP,5-278324,A and 7-81214 ] a rosary, or branched can be mentioned.

[0035] However, in order to obtain high glossiness and high void volume, it is desirable to use the silica ultrafine particle whose mean particle diameter is 7-30nm for the opening layer of the side separated especially from the base material. This silica particle may be the object which cation denaturation could be carried out in the front face, and was processed by aluminum, calcium, Mg, Ba, etc.

[0036] moreover, as a calcium carbonate preferably used for the ink jet record form of this invention For example, JP,57-12486,A, 57-129778, 58-55283, The precipitated calcium carbonate which has specific surface area in the specification indicated by 61-20792, The needle pillar-shaped calcium carbonate indicated by JP,63-57277,A \*\*\*\* JP,4-250091,A, The calcium-carbonate particle which the specific needlelike primary particle indicated by JP,3-251487,A condensed, and formed the secondary particle, the needle which has the specific oil absorption indicated by JP,4-250091,A and 4-260092 — a pillar-shaped prismatic crystal Argo night calcium carbonate, the spherical precipitated calcium carbonate indicated by JP,7-40648,A are mentioned.

[0037] It is desirable that particle size uses calcium-carbonate particle about 0.1 micrometers or less for the opening layer of the side separated especially from the base material, and it is desirable to use the calcium-carbonate particle especially whose mean particle diameter is 10-50nm.

[0038] Furthermore, in the opening layer of the side separated from the base material, the mean particle diameter of an alumina or hydrated alumina has desirable about 0.2 micrometers or less, especially the alumina or hydrated alumina preferably used for this invention has the pore whose radius it is 10-100nm and is 3-10nm, and it is especially desirable that they are the porosity alumina whose sum of this pore volume is 0.2 - 2 ml/g, or its hydrated compound. The measurement means of pore volume can be measured with a well-known nitrogen adsorption process to an alumina or the desiccation solid content of hydrated alumina.

[0039] An alumina or hydrated alumina may be crystallinity, or may be amorphous, and although a configuration can use the object of the configuration of arbitration, such as an infinite form particle, a spherical particle, and a fiber particle, in order to obtain high void volume, it is desirable to use a fibrous thing.

[0040] Moreover, the solid-state particle (B) of this invention has the desirable silica particle points, such as ink absorptivity and low cost, to whose secondary [ an average of ] particle size is 1-10 micrometers.

[0041] The above-mentioned opening layer of the ink jet record form of this invention needs to contain the hydrophilic binder, in order to maintain the property as a coat.

[0042] However, it is important for a hydrophilic binder to swell, to swell in the activity of a hydrophilic binder, at the time of the osmosis in early stages of ink, and not to take up an opening substantially, and a hydrophilic binder with low bloating tendency is comparatively used preferably near a room temperature from this viewpoint. Especially a desirable hydrophilic binder is the polyvinyl alcohol or cation denaturation polyvinyl alcohol of perfect or partial saponification, and is \*\*.

[0043] one especially desirable also in polyvinyl alcohol — whenever [ saponification ] — 80 or more parts — or full saponification is carried out. Moreover, from a viewpoint which improves coat brittleness, 500-3500 are desirable especially desirable, and, as for the average degree of polymerization of polyvinyl alcohol, the thing of 1000-3500 is used.

[0044] Moreover, it is polyvinyl alcohol which has the 1-3rd class amino group which is indicated by

JP,61-10483,A, for example, and the 4th class ammonium in the principal chain of the above-mentioned polyvinyl alcohol, or a side chain as cation denaturation polyvinyl alcohol.

[0045] Moreover, although other hydrophilic binders can be made to contain in said opening layer, as for those hydrophilic binders, it is preferably desirable that it is 20 or less % of the weight in general to the above-mentioned polyvinyl alcohol or cation denaturation polyvinyl alcohol.

[0046] Next, when forming the opening layer of the side which is separated from the opening layer of the ink jet record form of this invention, especially a base material, said approach (2) used preferably and (3) are further explained to a detail below.

[0047] It is good to carry out voidage preferably by said approach (2) more than 150 capacity %.

Although the upper limit of voidage generally changes with the class of bulking agent, or the classes of hydrophilic binder, generally it is below 200 capacity % from the reinforcement as a coat, brittleness, etc.

[0048] Especially in order to carry out voidage to more than 100 capacity %, the ratio of a solid-state particle and a hydrophilic binder is important, and it is desirable that the weight ratio to the hydrophilic binder of this solid-state particle carries out to 10 or more and less than 200 by this approach. This weight ratio becomes difficult [ it / for void volume to obtain 100% or more less than by ten ], and the brittleness of a coat deteriorates in the case of 200 or more.

[0049] In this case, it is desirable to use a calcium-carbonate particle, an aforementioned alumina, or an aforementioned hydrated alumina particle especially.

[0050] Said approach (3) is the approach of forming a flocculation condition and forming the network structure into a coat, and into the water solution which contains a hydrophilic binder preferably, the primary ultrafine particle in a distributed condition is formed via the condition of condensing each other, where a point of contact is restricted comparatively. that such a flocculation condition is linear or the condition that what formed floc in the shape of branching was distributed in the water solution — or the condition of such flocs condensing each other further and taking the three-dimension network structure in a water solution is included.

[0051] Even if it is which case, detailed structure can be formed into the formed coat by carrying out spreading desiccation of this water solution on a base material.

[0052] Thus, in general, from the magnitude of a primary particle, the magnitude of the detailed opening in the obtained coat is about several times those magnitude of this, and has the description which is the opening of detailed magnitude.

[0053] It is formed in the water solution which has the approach of being hard to condense a primary particle to each other, carrying out ultralow-volume addition of the hydrophilic polymer which accelerates condensation of a particle in the water solution containing the hydrophilic polymer which can exist in stability as an approach of forming such a flocculation condition, for example, and forming condensation slightly, or the water-soluble polymer which can perform a primary particle front face and weak coupling.

[0054] It is desirable from that the latter approach tends to form the amount of an opening in stability especially in this invention that it is comparatively easy to control, that more amounts of openings are obtained as compared with the amount of the particle to be used, and a coat with the still higher glossiness of a coat being obtained.

[0055] In this case, especially a desirable thing is the case where use said particle silica as a primary particle, and polyvinyl alcohol or cation denaturation polyvinyl alcohol is used as a hydrophilic binder. In this case, hydrogen bond with weak silanol group of a particle silica front face and hydroxyl group of vinyl alcohol is performed, and a flocculation object is formed.

[0056] The particle silica compounded by the synthetic approach called a gaseous-phase method especially as such a particle silica is used preferably.

[0057] By this approach, as a hydrophilic binder, as for especially the polymerization degree of the polyvinyl alcohol used preferably, 1000 or more are desirable, and it is desirable in order for 1500 especially or more to carry out for not causing a crack to a coat.

[0058] Here, the ratios of polyvinyl alcohol and the above-mentioned silica are 1:10-1:1 in general, and the range of them is 1:7-1:2 preferably.

[0059] It explains briefly [ below ] about the approach of forming the coat which contains a flocculation object using polyvinyl alcohol and a particle silica.

[0060] In the polyvinyl alcohol water solution (in general 5 – 15%) which maintained pH at 6–8, and the temperature of about 40 degrees C, it adds gradually, strong-agitating silica dispersion liquid (in general 5 – 15%), and an ultrasonic disperser, a high-speed homogenizer, etc. distribute after addition termination. In this case, various kinds of surfactants may be made to exist if needed. Subsequently, after adding various kinds of additives, it adjusts to target viscosity required for spreading, and the coat which has the above-mentioned opening by applying and drying by the well-known approach on a base material is obtained.

[0061] Although it is desirable in this invention to contain various kinds of oil droplets in order to improve the brittleness of a coat the solubility over water [ in / as such an oil droplet / a room temperature ] — about 0.01 or less % of the weight of a hydrophobic high-boiling point organic solvent (for example, a liquid paraffin —) dioctyl phthalate, tricresyl phosphate, a silicone oil, etc. and a polymer particle (for example, styrene —) The particle to which the polymerization of the one or more sorts was carried out for polymerization nature monomers, such as butyl acrylate, a divinylbenzene, butyl methacrylate, and hydroxyl ethyl methacrylate, can be made to contain. Such an oil droplet can be preferably used ten to 50% of the weight to a hydrophilic binder.

[0062] The sum total of the void volume of the opening layer of the ink jet record form of this invention is two or more [ 20ml //m / per two ] 1m of ink jet record forms. When the sum total of void volume is less than two 20 ml/m, although the absorptivity of the amount of low ink is good, ink overflows in the case of printing of the high amount of ink, image quality is reduced or problems, like drying [ after printing ] is late tend to generate it.

[0063] On the other hand, although especially the upper limit of the sum total of void volume is not restricted, the desiccation thickness of an opening layer is two or less 40 ml/m in general from it being required in order that making it 50 micrometers or less in general may not worsen the physical characteristic of coats, such as a crack.

[0064] Therefore, in order to attain the sum total of two or more 20 ml/m void volume, it is desirable to carry out voidage of an opening layer more than 100 capacity %.

[0065] Void volume is the value which deducted the total amount of the capacity of solid content, such as a binder in an opening layer, and various kinds of bulking agents, from the desiccation thickness in an opening layer, and voidage shows the rate of the amount of openings to the capacity of these solid content here.

[0066] It is the range which does not have an adverse effect on the effectiveness in this invention, and a bloating tendency ink absorption layer may be prepared. In this case, since it is required to show high bloating tendency to a liquid ink drop, the hydrophilic binder in which liquid ink bloating tendency is shown is used as a main configuration of this swelling layer. As a hydrophilic binder used preferably For example, gelatin or a gelatin derivative, a polyvinyl pyrrolidone (about 200,000 or more have desirable average molecular weight), A pullulan, polyvinyl alcohol or its derivative, a polyethylene glycol (100,000 or more have desirable average molecular weight), A carboxymethyl cellulose, hydroxyethyl cellulose, a dextran, A dextrin, polyacrylic acid and its salt, an agar, a kappa carrageenan, lambda-carrageenan, iota-carrageenan, xanthene gum, locust bean gum, A polyalkylene oxide system copolymerization nature polymer given in an alginic acid, gum arabic, a pullulan, JP,7-195826,A, and 7-9757, Polymers, such as independent or a copolymer which repeats and has these vinyl monomers of the vinyl monomer which has the carboxyl group and sulfonic group of a publication, can be mentioned to a water-soluble polyvinyl butyral or JP,62-245260,A. These hydrophilic binders may be used independently and may use two or more sorts together.

[0067] Since a swelling layer needs to have the early permeability and the bloating tendency over liquid ink, it contains at least one sort as which 200,000 or more polyvinyl pyrrolidones are chosen as for molecular weight, and about 50,000 or more polyethylene oxide and molecular weight are chosen for molecular weight from the copolymer of 100,000 or more polyethylene oxide and polypropylene oxide, hydroxyethyl cellulose, and polyacrylamide preferably as a hydrophilic binder of a swelling layer.

[0068] Moreover, it is desirable to use reversibly a part of hydrophilic binder in which sol gel transformation is possible from a viewpoint of stability high-speed spreading, and it is desirable from this point to use at least one sort of gelatin, a gelatin derivative, and a kappa carrageenan.

[0069] In this invention, various kinds of well-known surfactants can be used. In order to make the

flare degree of a liquid ink drop large comparatively, it is desirable to use the surfactant which generally lowers surface tension, and it is desirable to use an anion system surfactant and a fluorochemical surfactant especially.

[0070] Various kinds of additives can be made to contain if needed in the ink receptiveness layer of the arbitration of the ink jet record form of this invention.

[0071] For example, an ultraviolet ray absorbent given in JP,57-74193,A, 57-87988, and 62-261476, JP,57-74192,A, 57-87989, 60-72785, The fading inhibitor indicated by 61-146591, JP,1-95091,A, 3-13376, etc., An anion, a cation or the various surfactants of Nonion, JP,59-42993,A, The fluorescent brightener indicated by 59-52689, 62-280069, 61-242871, JP,4-219266,A, etc., Various well-known additives, such as lubricant, such as pH regulators, such as a sulfuric acid, a phosphoric acid, a citric acid, a sodium hydroxide, a potassium hydroxide, and potassium carbonate, a defoaming agent, and a JIECHIREN glycol, antiseptics, a thickener, a hardening agent, an antistatic agent, and a mat agent, can also be made to contain.

[0072] An inorganic or organic hardening agent can be used as a hardening agent, for example, chromium alum, formaldehyde, a glyoxal, an epoxy system compound, a vinyl sulfone system compound, an acryloyl system compound, s-triazine system compound, N-methylol system compound, a carbodiimide system compound, ethylene imino \*\*\*\*\* etc. can be used.

[0073] Into the configuration layer of the arbitration by the side of the ink recording surface of this invention, an alkali-metal weak acid salt the poly allylamine of publications, such as the poly cation polyelectrolyte of JP,56-84992,A, a basic latex polymer of JP,57-36692,A, JP,4-15744,B, JP,61-58788,A, and 62-174184, and given in JP,61-47290,A etc. can be used more than a kind as a deck-watertight-luminaire-ized agent of an image.

[0074] As a base material of the ink jet record form of this invention, a thing well-known as a record form for ink jets can be used suitably conventionally.

[0075] The thing of a property which bears the radiant heat when being able to mention the film which consists of ingredients, such as polyester system resin, diacetate system resin, triacetate system resin, acrylic resin, polycarbonate system resin, polyvinyl chloride system resin, polyimide system resin, cellophane, and celluloid, a plate, a glass plate, etc. as a transparency base material, for example, and being used as an OHP also in this is desirable, and especially polyethylene terephthalate is desirable. As thickness of such a transparent base material, about 10-200 micrometers is desirable.

[0076] Moreover, although what carried out opacification processing of the sheet which consists of common paper, a synthetic paper, resin coat paper, cloth, timber, a metal, etc. as a base material to be used, for example, a plate, and the above-mentioned translucency base material with the well-known means can be mentioned when there is no transparent need The so-called White pet which comes to add white pigments to the resin coat paper (the so-called RC paper) which has the polyolefin resin enveloping layer which added white pigments etc. at least to one side of a base paper, and polyethylene terephthalate is desirable. It is desirable to perform corona discharge treatment, undercoating processing, etc. to a base material in advance of spreading of an ink absorbing layer for the object, such as to enlarge bond strength of a base material and an ink television layer. Furthermore, the ink jet record form of this invention does not necessarily need to be colorlessness, and may be a colored ink jet record form.

[0077] Also in these, as a base material of this invention, a hydrophobic base material is desirable, for example, are polyethylene terephthalate, polyolefin resin coat paper, and the White pet.

[0078] Although it can carry out by choosing suitably the approach of applying the layer containing the non-subtlety particle of this invention on a base material from a well-known approach, the extrusion coat method which uses a hopper the roll coat method, the rod bar coat method, the air knife coat method, a spray coating method, the curtain coat method, or given in a U.S. Pat. No. 2681294 official report is used preferably.

[0079] Moreover, after it cools and the gel state takes after applying on a base material as indicated by JP,6-64306,A in using the hydrophilic binder in which sol gel transformation, such as gelatin, and a gelatin derivative, a kappa carrageenan, is possible, you may carry out by the approach of drying by the cold dry cleaning method.

[0080] In case image recording is carried out using the ink jet record form of this invention, the

record approach which used water color ink is used.

[0081] The ink jet recording ink (only henceforth ink jet recording ink) containing the water soluble dye said by this invention is the following water soluble dye and a solvent object, and recording ink that consists of other additives. Water soluble dye, such as direct dye well-known as water soluble dye at an ink jet, acid dye, basic dye, reactive dye, or a food dye, can be used.

[0082] As a solvent of ink jet recording ink, water and water-soluble, various organic solvents, For example, methyl alcohol, isopropyl alcohol, n-butyl alcohol, Alcohols, such as tert-butyl alcohol and isobutyl alcohol; Dimethylformamide, Amides, such as dimethylacetamide; Ketones, such as an acetone and diacetone alcohol, or a ketone-alcohol; tetrahydrofuran, Ether, such as dioxane; Polyalkylene glycols; ethylene glycol, such as a polyethylene glycol and a polypropylene glycol, Propylene glycol, a butylene glycol, triethylene glycol, 1, 2, 6-hexane triol, thiodiglycol, hexylene glycol, Polyhydric alcohol, such as a diethylene glycol, a glycerol, and triethanolamine; Ethylene glycol methyl ether, The low-grade alkyl ether of polyhydric alcohol, such as the diethylene-glycol methyl (or ethyl) ether and the triethylene glycol monobutyl ether, is mentioned.

[0083] Also in the water-soluble organic solvent of these many, the low-grade alkyl ether of the polyhydric alcohol of polyhydric alcohol, such as a diethylene glycol, triethanolamine, and a glycerol, and the triethylene glycol monobutyl ether etc. is desirable.

[0084] As an additive of other ink jet recording ink, pH modifier, a sequestering agent, an antifungal agent, a viscosity controlling agent, a surface tension regulator, a wetting agent, a surfactant, a rusr-proofer, etc. are mentioned, for example.

[0085] In order that the wettability to an ink jet record form may make it good, in 20 degrees C, ink jet recording ink has desirable 25 – 60 dyn/cm, and it is desirable to have the surface tension of 30 – 50 dyn/cm within the limits more preferably.

[0086] the ink jet recording method in which the regurgitation [ ink jet recording ink ] of the ink regurgitation method at the time of carrying out image recording using the ink jet record form of this invention is possible — it is — \*\*\*ing — for example, "ink jet record technical trend" Nakamura [ Koichi ] editing — recording methods, such as a continuation injection electrification control system, a method on demand, etc. of a publication, can be used for work (Japanese Science-information, 1995) p.1-14. However, bigger effectiveness can be acquired by using it also in these, applying to the recording method of a method on demand.

[0087] The ink maximum delivery in this invention is the maximum of the amount of ink volume per [ which can be used when the ink jet printer used for this invention outputs all the usual images ] unit volume. For example, it is not necessarily the ink maximum delivery which added the amount of ink for obtaining the maximum density of yellow, Magenta, cyanogen, and black each monochrome in the case of the printer for color pictures. An ink maximum delivery can be calculated by count, if the volume of one drop of ink jet recording ink is known and the array approach of the drop for forming an image is known.

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[Translation done.]

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EXAMPLE

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[Example] Although the example of this invention is given and explained below, this invention is not limited to these examples. In addition, in an example, especially, as long as there is no notice, oven-dry-weight % is shown "%."

[0089] To the recording surface side on the paper base material (in the polyethylene layer by the side of 140 micrometers in thickness, and a recording surface, anatase mold titanium-dioxide content is carried out, and it has 7% of the weight of the layer which contains alkali treatment gelatin 1.2 g/m<sup>2</sup> and a hardening agent as a back layer in the rear-face side of a recording surface) which covered 1100g of examples/, and stencil both sides of m<sup>2</sup> with polyethylene, it applied and the following [coating liquid -1] was dried so that humid thickness might turn to 125 micrometers.

[0090]

[Coating liquid -1]

Pure water 980ml Particle silica with a mean particle diameter of about 2.5 micrometers 48.2g Polyvinyl alcohol of average degree of polymerization 1700 (whenever [ saponification ] 90%) 24.1g Surfactant -1 1.2g [0091]

[Formula 1]

界面活性剤-1



[0092] Subsequently, the coating liquid -2 of the following presentations was applied by 100 micrometers of humid thickness on this spreading layer, it dried, and the ink jet record form -1 of this invention was obtained. Thus, the sum total of the void volume of the obtained coat was 24 ml/m<sup>2</sup>.

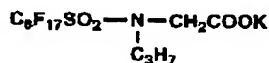
[0093]

[Coating liquid -2]

Pure water 980ml Particle silica with a mean particle diameter of about 7nm 48.2g Polyvinyl alcohol of average degree of polymerization 3500 (whenever [ saponification ] 90%) 16.1g Surfactant -2 1.2g [0094]

[Formula 2]

界面活性剤-2



[0095] Next, ink jet record form which changed coating liquid as follows respectively using [ on the ink jet record form -1 and ] [coating liquid -1] and [coating liquid -2] - 2-10 were created like the ink jet record form -1.

[0096] Ink jet record form - It is the same as the ink jet record form -1 except having not applied 2: [coating liquid -2], but [coating liquid -1] having performed spreading twice by 125 micrometers of humid thickness. (The sum total of void volume = about 25 ml/m<sup>2</sup>)

Ink jet record form - It is the same as the ink jet record form -1 except having applied the humid

thickness of 3: [coating liquid -1] by 140 micrometers of humid thickness of 80 micrometers and [coating liquid -2]. (The sum total of void volume = about 24 ml/m<sup>2</sup>)

Ink jet record form - It is the same as the ink jet record form -1 except having used the silica with a mean particle diameter of 1.4 micrometers instead of the silica with a mean particle diameter [ of 4: [coating liquid -1] ] of 2.5 micrometers. (The sum total of void volume = about 23 ml/m<sup>2</sup>)

Ink jet record form - It is the same as the ink jet record form -1 except having used the colloid silica with a mean particle diameter of 0.1 micrometers instead of the silica with a mean particle diameter [ of 5: [coating liquid -1] ] of 2.5 micrometers. (The sum total of void volume = about 21 ml/m<sup>2</sup>)

Ink jet record form - After changing the surfactant of 2 and [coating liquid -2] into 1 for the surfactant of 6: [coating liquid -1] and applying [coating liquid -2], it is the same as the ink jet record form -1 except having applied [coating liquid -1]. (The sum total of void volume = about 24 ml/m<sup>2</sup>)

Ink jet record form - It is the same as the ink jet record form -1 except having performed each humid thickness of 7: [coating liquid -1] and [coating liquid -2] by 80 micrometers. (The sum total of void volume = about 16 ml/m<sup>2</sup>)

Ink jet record form - The mean particle diameter of 8 micrometers is the same as the ink jet record form -1 instead of a particle silica with a mean particle diameter [ of 8: [coating liquid -1] ] of 2.5 micrometers except having used the particle silica. (The sum total of void volume = about 23 ml/m<sup>2</sup>)

Ink jet record form - The mean particle diameter of 12 micrometers is the same as the ink jet record form -1 instead of a particle silica with a mean particle diameter [ of 9: [coating liquid -1] ] of 2.5 micrometers except having used the particle silica. (The sum total of void volume = about 24 ml/m<sup>2</sup>)

Ink jet record form - The mean particle diameter of 7nm of 10: [coating liquid -2] is the same as the ink jet record form -1 except having used the colloid child silica with a mean particle diameter of 50nm instead of the particle silica. (The sum total of void volume = about 23 ml/m<sup>2</sup>)

About each obtained ink jet record form, using ink jet printer MJ[ by Seiko Epson, Inc. ]-5100C, the assessment pattern was printed and the following items were evaluated.

[0097] (1) Ink absorption capacity : when 30% of the amount of the maximum ink of \*\* yellow, 60% of regurgitation of the amount of the maximum ink of each ink of cyanogen, and Magenta ink was made to breathe out at the time of 60% of regurgitation of the amount of the maximum ink of each ink of \*\* yellow and cyanogen, the condition of the overflow of the ink in each case was observed visually.

[0098] [The overflow of ink]

O x dried within about 10 seconds although it is overflowing slightly immediately after \*\*:printing which does not overflow at all immediately after :printing : it takes a front face 10 seconds or more to overflow immediately after printing and to dry.

[0099] (2) Ink absorptivity : homogeneity was made to breathe out and it recorded so that it might become 30% of the amount of the maximum ink, respectively, and 20 red-reflex concentration of the solid section was measured using the microdensitometer (aperture =200micrometerphi), and the value of \*\* yellow and cyanogen broken by average reflection density in quest of the standard deviation of the variation in the concentration was calculated. When ink absorptivity is good, the value of non-Lycium chinense becomes [ nonuniformity ] small at an image, but if ink absorptivity falls, this each other liquid ink drops will cause beading mutually in the ink jet record paper, it will become nonuniformity, and this value will increase.

[0100] (3) Drying : time amount until it leaves a regular paper in piles and ink stops imprinting 60% printing section of yellow and a Magenta in a regular paper after after [ printing ] fixed time amount progress was found.

[0101] (4) Dot diameter : the single dot of black was printed in the single dot diameter (K) of black ink, and the yellow solid printing section, and they were observed and asked for the diameter under the microscope (K/Y). The diameter measured the area of 20 dots, respectively and asked for this as the average of the diameter when carrying out circle conversion. (Unit: micrometer)

(5) Glossiness : gloss was measured for the printing side 75 degrees using the deflection

glossmeter (VGS-1001DP) by Nippon Denshoku Industries Co., Ltd.

[0102] The obtained result is shown in a table 1.

[0103]

[A table 1]

インクジェット 記録用紙	インク吸収容量		インク吸収性	乾燥性	ドット直徑		光沢度 (%)
	①	②			K	K/Y	
1 (本発明)	○	○	0.09	2分	80	110	66
2 (比較例)	○	○	0.06	1分	100	150	5
3 (本発明)	○	○	0.10	2分	80	110	67
4 (本発明)	○	○	0.10	2分	90	110	70
5 (比較例)	○	△	0.13	3分	90	130	72
6 (比較例)	○	○	0.07	1分	100	140	8
7 (比較例)	△	×	0.18	4分	60	(a)	68
8 (本発明)	○	△	0.09	2分	80	110	60
9 (本発明)	○	○	0.09	2分	80	110	51
10 (本発明)	○	○	0.11	2分	90	110	68

(a) 測定不能

[0104] Ink jet record form of the result of a table 1 to this invention – It turns out that 1, 3, 4, and 8 have a high ink absorption capacity, good ink absorptivity, and glossiness high in a drying list, and dot size is small suitable for high definition ink jet record. On the other hand, although ink absorptivity and drying are good, glossiness falls substantially, and even if dot size is large and moreover micrifies a liquid ink drop, a high-definition image can obtain easily neither the ink jet record form –6 which used the big particle of a mean diameter for the side separated from the base material, nor the ink jet record form –2 only using the big particle of a mean diameter.

[0105] As for the ink jet record form –5 using the small particle of the mean diameter of the particle of a side far from a base material, lowering of ink absorptivity is seen at the side near a base material. The sum total of void volume is small, ink absorption capacity was lacking and the high-definition image was not obtained for the ink jet record form –7.

[0106] Moreover, ink jet record form of this invention using the big particle of a larger mean diameter than the particle contained in the ink jet record form which is the desirable mode of this invention – 9 and 10 are compared with the ink jet record form which is the desirable mode of this invention, and its glossiness is low a little.

[0107] It is an ink jet record form like an example 1 except having changed [coating liquid –2] into the following [coating liquid-2a] in example 2 example 1. – It is the ink jet record form of a configuration like 1-7. – 21-27 were created and it evaluated like the example 1.

[0108]

[Coating liquid-2a]

Pure water 960ml Particle calcium carbonate (mean particle diameter = about 0.03 micrometers) 76.9g Polyvinyl alcohol of average degree of polymerization 1700 (whenever [ saponification ] 90%) 9.6g Surfactant –1 1.2g of ink jet record forms –28 as well as the ink jet record form –21 was created again except having used the particle calcium carbonate with a mean particle diameter of 0.07 micrometers instead of the particle calcium carbonate with a mean particle diameter [ of [coating liquid-2a] ] of 0.03 micrometers.

[0109] The object for openings and swelling layer membrane thickness of each ink jet record form were as follows.

[0110] Ink jet record form – 21: sum total [ of void volume ] = — about 26 ml/m<sup>2</sup> ink-jet record form-22: — sum total [ of void volume ] = — about 25ml/[m] 2 ink-jet record form-23: — sum total [ of void volume ] = — about 25 ml/m<sup>2</sup> ink-jet record form-24: — sum total [ of void volume ] = — about 25ml /m<sup>2</sup> ink-jet record form – 25: sum total [ of void volume ] = — about 23 ml/m<sup>2</sup> ink-jet record form-26: — sum total [ of void volume ] = — about 26 ml/m<sup>2</sup> ink-jet record form-27 : sum total [ of void volume ] = — about 19 ml/m<sup>2</sup> ink-jet record form-28: — sum total [ of void volume ] = — the ink jet record form of about 25 ml/m<sup>2</sup> \*\* The same assessment as an example 1 is performed, and a result is shown in a table 2.

[0111]

[A table 2]

インクジェット 記録用紙	インク吸収容量		インク吸収性	乾燥性	ドット直径		光沢度 (%)
	①	②			K	K/Y	
21 (本発明)	○	○	0.11	2分	90	110	68
22 (比較例)	○	○	0.06	1分	100	150	5
23 (本発明)	○	○	0.12	2分	90	110	72
24 (本発明)	○	○	0.12	2分	90	110	71
25 (比較例)	○	△	0.14	3分	90	120	74
26 (比較例)	○	○	0.07	1分	100	140	9
27 (比較例)	○	△	0.19	4分	60	(a)	68
28 (本発明)	○	○	0.13	3分	90	120	61

(a) 測定不能

[0112] Even if it changes to a particle silica and transposes to a particle calcium carbonate as an inorganic bulking agent from the result of a table 2, it turns out that the same effectiveness as an example 1 is acquired.

[0113] It is an ink jet record form like an example 1 except having changed [coating liquid-2] into the following [coating liquid-2bs] in example 3 example 1. - It is the ink jet record form of a configuration like 1-7. - 31-37 were created and it evaluated like the example 1.

[0114]

[Coating liquid-2b]

Pure water 200ml Alumina sol (catalyst formation the product made from Industry, Cataloid AS-3) 750ml Polyvinyl alcohol of average degree of polymerization 1700 (whenever [ saponification ] 90%) 7.6g Surfactant -1 Except having used the alumina of 1 micrometer of mean diameters instead of the alumina sol of [coating liquid-2b], the ink jet record form -38 as well as the ink jet record form -31 was created, and 1.2g was evaluated like the example 1 again.

[0115] The object for openings and swelling layer membrane thickness of each ink jet record form were as follows.

[0116] Ink jet record form - 31: sum total [ of void volume ] = — about 22 ml/m<sup>2</sup> ink-jet record form-32: — sum total [ of void volume ] = — about 25 ml/m<sup>2</sup> ink-jet record form-33: — sum total [ of void volume ] = — about 22 ml/m<sup>2</sup> ink-jet record form-34: — sum total [ of void volume ] = — an about 21 ml/m<sup>2</sup> ink-jet record form - 35: — sum total [ of void volume ] = — about 21ml /m<sup>2</sup> ink-jet record form-36: — sum total [ of void volume ] = — about 24 ml/m<sup>2</sup> ink-jet record form-37: — sum total [ of void volume ] = — about 15 ml/m<sup>2</sup> ink-jet record form-38: — sum total [ of void volume ] = — about 21 ml/m<sup>2</sup> result It is shown in a table 3.

[0117]

[A table 3]

インクジェット 記録用紙	インク吸収容量		インク吸収性	乾燥性	ドット直径		光沢度 (%)
	①	②			K	K/Y	
31 (本発明)	○	○	0.11	2分	70	100	70
32 (比較例)	○	○	0.06	1分	100	150	5
33 (本発明)	○	○	0.12	2分	70	100	71
34 (本発明)	○	○	0.10	2分	70	100	72
35 (比較例)	○	△	0.11	3分	70	100	73
36 (比較例)	○	○	0.07	1分	90	130	8
37 (比較例)	△	×	0.21	5分	80	(a)	71
38 (本発明)	○	○	0.13	3分	80	140	62

(a) 測定不能

[0118] Even if it changes to a particle silica and transposes to particle alumina sol as an inorganic bulking agent from the result of a table 3, it turns out that the same effectiveness as an example 1 is acquired.

[0119] Although it was opaque and the case where a glossy paper base material was used was explained by this example, the suitable ink jet record form for the application using transparency of CFM used for color displays, such as the color-separation version at the time of creating what observes a record image by projection to a screen etc., and the positive version of color printing by optical instruments, such as a slide and OHP, or liquid crystal, can be offered by using a

transparent base material.

[0120] Moreover, although the case where it mainly uses for an ink jet method has been explained about the ink jet record form of this invention, it can use suitable for record by record devices, such as various writing materials, a pen plotter, etc. which use water color ink besides an ink jet method.

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(54)【発明の名称】 インクジェット記録用紙及びこれを用いたインクジェット記録方法

(57)【要約】

【課題】 水性インクによる印字において、高いインク吸収性を有し、かつ、高い光沢度や透明性を有した、高品位の画像形成を可能にしたインクジェット記録用紙及びこれを用いたインクジェット記録方法の提供。

【解決手段】 支持体上に固体微粒子と親水性バインダーを含有する少なくとも2層の空隙層を設けてなるインクジェット記録用紙において、支持体より離れた側の空隙層に含有する固体微粒子(A)の平均粒径が、支持体より近い側の空隙層に含有する固体微粒子(B)の平均粒径より小さく、かつ前記空隙層の空隙容量の合計が20m<sup>1</sup>/m<sup>2</sup>以上であることを特徴とするインクジェット記録用紙。

## 【特許請求の範囲】

【請求項1】 支持体上に固体微粒子と親水性バインダーを含有する少なくとも2層の空隙層を設けてなるインクジェット記録用紙において、支持体より離れた側の空隙層に含有する固体微粒子(A)の平均粒径が、支持体より近い側の空隙層に含有する固体微粒子(B)の平均粒径より小さく、かつ前記空隙層の空隙容量の合計が $20\text{ ml/m}^2$ 以上であることを特徴とするインクジェット記録用紙。

【請求項2】 前記支持体が疎水性支持体であることを特徴とする請求項1に記載のインクジェット記録用紙。

【請求項3】 前記固体微粒子(A)が、平均粒径7~30nmのシリカ系微粒子であることを特徴とする請求項1又は2に記載のインクジェット記録用紙。

【請求項4】 前記固体微粒子(A)が平均粒径10~50nmの炭酸カルシウム微粒子であることを特徴とする請求項1又は2に記載のインクジェット記録用紙。

【請求項5】 前記固体微粒子(A)が平均粒径10~100nmのアルミナ又はアルミナ水和物微粒子であることを特徴とする請求項1又は2に記載のインクジェット記録用紙。

【請求項6】 前記固体微粒子(B)が、平均2次粒径1~10μmのシリカ系微粒子であることを特徴とする請求項1~5の何れか1項に記載のインクジェット記録用紙。

【請求項7】 前記親水性バインダーの少なくとも1種がポリビニルアルコール又はカチオン変性ポリビニルアルコールであることを特徴とする請求項1~6の何れか1項に記載のインクジェット記録用紙。

【請求項8】 請求項1~7の何れか1項に記載のインクジェット記録用紙に、水溶性染料を含有するインクジェット記録液を用い最大吐出インク量が $20\text{ ml/m}^2$ 以上となる条件で印字することを特徴とするインクジェット記録方法。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 本発明は、水性インクを用いて記録を行うインクジェット記録用紙及びこれを用いたインクジェット記録方法に関し、更に詳しくはインク吸収性、光沢性に優れたインクジェット記録用紙及びこれを用いたインクジェット記録方法に関するものである。

## 【0002】

【従来の技術】 インクジェット記録は、インクの微小液滴を種々の作動原理により飛翔させて紙などの記録シートに付着させ、画像・文字などの記録を行うものであるが、比較的高速、低騒音、多色化が容易である等の利点を有している。この方式で従来から問題となっていたノズルの目詰まりとメンテナンスについては、インク及び装置の両面から改良が進み、現在では各種プリンター、ファクシミリ、コンピューター端末等、さまざまな分野

に急速に普及している。

【0003】 このインクジェット記録方式で使用されるインクジェット記録用紙としては、印字ドットの濃度が高く、色調が明るく鮮やかであること、インクの吸収が早く印字ドットが重なった場合に於いてもインクが流れ出したり滲んだりしないこと、印字ドットの横方向への拡散が必要以上に大きくなく、かつ周辺が滑らかでぼやけないこと等が要求される。

【0004】 特にインク吸収速度が遅い場合には、2色以上のインク液滴が重なって記録される際に、インクジェット記録用紙上で液滴がハジキ現象を起こしてムラになったり、また、異なる色の境界領域でお互いの色が滲んだりして画質を大きく低下させやすいために、インクジェット記録用紙としては高いインク吸収性を持たせるようになることが必要である。

【0005】 これらの問題を解決するために、従来から非常に多くの技術が提案されている。

【0006】 例えば、特開昭52-53012号に記載されている低サイズ原紙に表面加工用の塗料を湿潤させたインクジェット記録用紙、特開昭55-5830号に記載されている支持体表面にインク吸収性の塗層を設けたインクジェット記録用紙、特開昭56-157号に記載されている被覆層中の顔料として非膠質シリカ粉末を含有するインクジェット記録用紙、特開昭57-107878号に記載されている無機顔料と有機顔料を併用したインクジェット記録用紙、特開昭58-110287号に記載されている2つの空孔分布ピークを有するインクジェット記録用紙、特開昭62-111782号に記載されている上下2層の多孔質層からなるインクジェット記録用紙、特開昭59-68292号、同59-123696号及び同60-18383号などに記載されている不定形亀裂を有するインクジェット記録用紙、特開昭61-135786号、同61-148092号及び同62-149475号等に記載されている微粉末層を有するインクジェット記録用紙、特開昭63-252779号、特開平1-108083号、同2-136279号、同3-65376号及び同3-27976号等に記載されている特定の物性値を有する顔料や微粒子シリカを含有するインクジェット記録用紙、特開昭57-14091号、同60-219083号、同60-210984号、同61-20797号、同61-188183号、特開平5-51470号、同5-278324号、同6-92011号、同6-183134号、同7-137431号、同7-276789号等に記載されているコロイド状シリカ等の微粒子シリカを含有するインクジェット記録用紙、及び特開平2-276671号、同3-67684号、同3-215082号、同3-251488号、同4-67986号、同4-263983号及び同5-16517号などに記載されているアルミナ水和物微粒子を含有するインクジェット記録用

紙等が多数知られている。

【0007】しかし、インク受容層がインクを吸収したり保持するための空隙を多く有する層のみから構成される場合、空隙の多いインク受容層が空気との界面や皮膜表面のミクロな凹凸を多く有することになり、インク受容層への入射光が散乱されたり、透過が妨げられるために、光沢が出にくくなったり不透明になりやすい。

【0008】また、空隙を形成するため顔料自身の凹凸や顔料の2次凝集体の凹凸による皮膜表面の平滑性が低下して光沢が出にくい欠点がある。

【0009】そこで光沢を付与する目的で特開平7-101142号にはインク受理層に主成分として無定形シリカアルミナに代表される平均粒子径300nm以下のコロイド粒子からなる光沢発現層を順次積層、同7-117335号にはこの後更にカレンダー処理することによって、高い光沢度を付与する技術が開示されているが、この方法ではインク吸収性と光沢度が取り合いとなり、充分とはいえない。

【0010】更に、空隙に浸透したインクに光が到達しにくくなるため画像が白っぽくなり、色再現性及び色濃度が低下する等の欠点を有しており、空隙の多いインク受容層で高い光沢性や透明性を維持しつつ、色再現性や色濃度の高い画像を得るのは困難であった。

#### 【0011】

【発明が解決しようとする課題】本発明は上記の実態に鑑みてなされたものであって、本発明の目的は、水性インクによる印字において、高いインク吸収性を有し、かつ、高い光沢度や透明性を有した、高品位の画像形成を可能にしたインクジェット記録用紙及びこれを用いたインクジェット記録方法を提供することにある。

#### 【0012】

【課題を解決するための手段】本発明の上記目的は以下の構成により達成される。

【0013】1. 支持体上に固体微粒子と親水性バインダーを含有する少なくとも2層の空隙層を設けてなるインクジェット記録用紙において、支持体より離れた側の空隙層に含有する固体微粒子(A)の平均粒径が、支持体より近い側の空隙層に含有する固体微粒子(B)の平均粒径より小さく、かつ前記空隙層の空隙容量の合計が20ml/m<sup>2</sup>以上であることを特徴とするインクジェット記録用紙。

【0014】2. 前記支持体が疎水性支持体であることを特徴とする前記1に記載のインクジェット記録用紙。

【0015】3. 前記固体微粒子(A)が、平均粒径7~30nmのシリカ系微粒子であることを特徴とする前記1又は2に記載のインクジェット記録用紙。

【0016】4. 前記固体微粒子(A)が平均粒径10~50nmの炭酸カルシウム微粒子であることを特徴とする前記1又は2に記載のインクジェット記録用紙。

【0017】5. 前記固体微粒子(A)が平均粒径10

~100nmのアルミナ又はアルミナ水和物微粒子であることを特徴とする前記1又は2に記載のインクジェット記録用紙。

【0018】6. 前記固体微粒子(B)が、平均2次粒径1~10μmのシリカ系微粒子であることを特徴とする前記1~5の何れか1項に記載のインクジェット記録用紙。

【0019】7. 前記親水性バインダーの少なくとも1種がポリビニルアルコール又はカチオン変性ポリビニルアルコールであることを特徴とする前記1~6の何れか1項に記載のインクジェット記録用紙。

【0020】8. 前記1~7の何れか1項に記載のインクジェット記録用紙に、水溶性染料を含有するインクジェット記録液を用い最大吐出インク量が20ml/m<sup>2</sup>以上となる条件で印字することを特徴とするインクジェット記録方法。

【0021】以下、本発明を詳細に説明する。

【0022】本発明のインクジェット記録用紙が有する空隙層は親水性のバインダーと無機又は有機の固体微粒子との間に形成される空隙から成る。

【0023】以下に固体微粒子による代表的な空隙の形成方法を説明する。

【0024】(1) 多孔質固体微粒子と親水性バインダーを含有する塗布液を支持体上に塗布し、多孔質微粒子内や粒子間に空隙を形成する方法、(2) 親水性バインダーに対して概ね等量以上(好ましくは1.0倍以上)の容積を有する固体微粒子と親水性バインダーを含有する塗布液を支持体上に塗布して固体微粒子の間に空隙を作成する方法、(3) 平均粒径が約0.1μm程度以下の固体微粒子を塗布液調製時又は皮膜形成時に凝集させて2次粒子又は3次元構造を形成して空隙を作成する方法。

【0025】本発明のインクジェット記録用紙における空隙形成方法は前記の何れの方法によても良いが、インクジェット記録用紙の光沢度をあまり低下させない方法を用いることが好ましい。一般に方法(1)は、インク吸収性に優れ、従来よりコート紙等で広く用いられているが、多孔質固体微粒子は合成不定形シリカに代表されるようにほとんどが2次凝集しているミクロンオーダーの粒子径の大きな粒子で、この方法で得られた空隙層だけでは十分な光沢性を得ることは困難であった。

【0026】インクジェット記録紙の最表面に親水性バインダーからなる膨潤層を形成させることによって、前記膨潤層を被覆していない状態では空隙層自体の光沢が多少低い場合であっても、表面膨潤層の存在により高い光沢性を付与することができる。しかし、空隙層の凹凸のサイズがあまりに大きすぎる場合には膨潤層による高い光沢性付与は困難になり、また、この膨潤層に一時的に吸収されたのち下層の空隙層に吸収されるため、インクの吸収速度が表面膨潤層へのインクの吸収速度が律速

となり遅くなる。表面光沢性向上のためこの表面膨潤層を厚くすればするほどこの傾向は強くなり、インクの吸収性は実質的に全体があたかも膨潤層である時と同程度の吸収性しか示さなくなってしまう。

【0027】そこで、本発明においては、支持体上に少なくとも2層の固体微粒子を含有する空隙層を設け、支持体から離れた側の層に含有する固体微粒子(A)の平均粒径が、支持体より近い側の層に含有する固体微粒子(B)の平均粒径に比べ小さい粒子を使用した空隙層を設けることにより、高いインク吸収性を維持したまま、高い光沢性を付与できることを見出した。

【0028】ここで、固体微粒子(A)の平均粒径は固体微粒子(B)のそれに比べ小さければ良いが、好ましくは1/5、より好ましくは1/10である。

【0029】本発明のインクジェット記録用紙のインク吸収のための空隙層の形成に好ましい方法としては、上記(2)ないし(3)を支持体から離れた側(上層)の空隙層として用いることである。

【0030】また2層の空隙層の間に中間層として膨潤層を設けると、インク吸収速度はこの中間膨潤層が律速となって、バインダー組成や厚みによっては遅くなることがあり、前記固体微粒子(A)を含有する層と前記固体微粒子(B)を含有する層が隣接していることが好ましい。

【0031】インク吸収層が固体微粒子を含有する空隙層で有る場合、固体微粒子としては従来インクジェット記録用紙で公知の各種の無機又は有機の固体微粒子を用いることが出来る。用いられる無機微粒子の例としては、軽質炭酸カルシウム、重質炭酸カルシウム、炭酸マグネシウム、カオリン、クレー、タルク、硫酸カルシウム、硫酸バリウム、二酸化チタン、酸化亜鉛、水酸化亜鉛、硫化亜鉛、炭酸亜鉛、ハイドロタルサイト、珪酸アルミニウム、ケイソウ土、珪酸カルシウム、珪酸マグネシウム、合成非晶質シリカ、気相法シリカ、コロイダルシリカ、アルミナ、コロイダルアルミナ、擬ペーマイト、水酸化アルミニウム、リトポン、ゼオライト、水酸化マグネシウム等の白色無機顔料等を挙げることが出来る。

【0032】一方有機微粒子の例としては、ポリスチレン、ポリアクリル酸エステル類、ポリメタクリル酸エステル類、ポリアクリルアミド類、ポリエチレン、ポリプロピレン、ポリ塩化ビニル、ポリ塩化ビニリデン、又はこれらの共重合体、尿素樹脂、又はメラミン樹脂等が挙げられる。

【0033】高い濃度を達成し、鮮明な画像を記録しコストで製造できる等の点から、本発明の固体微粒子(A)は、シリカ微粒子、炭酸カルシウム及びアルミナ水和物微粒子から選ばれる固体微粒子を用いることが好ましい。

【0034】本発明に好ましく使用されるシリカ系微粒

子としては従来インクジェットで公知の各種のシリカ系微粒子を使用することが出来、例えば、湿式又は気相法で合成された合成シリカ、コロイダルシリカ、1次粒子が凝集して2次粒子を形成している多孔質シリカ任意の形状のシリカを使用することが出来る。その様な例として、例えば特開昭55-51583号及び同56-148583号等に記載された合成非晶質シリカ、例えば特開昭60-204390号に記載された気相法により合成されたシリカ超微粒子、特開昭60-222282号に記載されたフッ素を含有する合成不定形シリカ、特開昭60-224580号及び同62-178384号に記載されたシランカップリング剤により表面処理された合成不定形シリカ、例えば特開昭62-183382号及び同63-104878号に記載された球状シリカ、特開昭63-317381号に記載されたNa<sub>2</sub>O含有量が0.5重量%以上である合成シリカ微粒子、特開平1-115677号に記載された比表面積が100m<sup>2</sup>/g以上の合成シリカ微粒子、特開昭62-286787号に記載されたアルミナ表面処理された合成シリカ微粒子、特開平1-259982号に記載されたCa、Mg又はBaで表面処理された合成シリカ微粒子、吸油量が180ml/g以上の合成シリカ微粒子、特開昭57-14091号に記載されたコロイダルシリカ、特開昭60-219084号、特開平6-92011号、同6-297830号及び同7-81214号に記載されたカチオン性コロイダルシリカ、及び特開平5-278324号及び同7-81214号に記載された数珠状に連結した又は分岐したコロイダルシリカ等を挙げることが出来る。

【0035】しかしながら、高い光沢性と高い空隙容量を得るため、特に支持体より離れた側の空隙層には、平均粒径が7~30nmのシリカ超微粒子を用いることが好ましい。このシリカ微粒子は表面をカチオン変性されたものであってもよく、また、Al、Ca、Mg及びBa等で処理された物であってもよい。

【0036】また、本発明のインクジェット記録用紙に好ましく用いられる炭酸カルシウムとしては、例えば、特開昭57-12486号、同57-129778号、同58-55283号、同61-20792号に記載された特定に比表面積を有する軽質炭酸カルシウム、特開昭63-57277号および特開平4-250091号に記載された針柱状炭酸カルシウム、特開平3-251487号に記載された特定の針状1次粒子が凝集して2次粒子を形成した炭酸カルシウム微粒子、特開平4-250091号及び同4-260092号に記載された特定の吸油量を有する針柱状の斜方晶アルゴナイト炭酸カルシウム、及び特開平7-40648号に記載された球状沈降性炭酸カルシウム等が挙げられる。

【0037】特に支持体より離れた側の空隙層には、粒径が約0.1μm以下の炭酸カルシウム微粒子を使用す

ることが好ましく、特に平均粒径が10～50nmの炭酸カルシウム微粒子を使用することが好ましい。

【0038】更に、本発明に好ましく用いられるアルミナ又はアルミナ水和物は、特に支持体より離れた側の空隙層には、アルミナ又はアルミナ水和物の平均粒径が約0.2μm以下が好ましく、特に10～100nmで、半径が3～10nmの細孔を有し、この細孔容積の和が0.2～2ml/gである多孔質アルミナ又はその含水物であることが好ましい。細孔容積の測定手段は、アルミナ又はアルミナ水和物の乾燥固体分に対して公知の窒素吸着法により測定することが出来る。

【0039】アルミナ又はアルミナ水和物は結晶性であっても、非晶質であっても良く、また、形状は不定形粒子、球状粒子、纖維状粒子など任意の形状の物を使用することが出来るが、高い空隙容量を得るために、纖維状のものを用いることが好ましい。

【0040】また、本発明の固体微粒子(B)は、インク吸収性、低コスト等の点から平均2次粒径が1～10μmのシリカ微粒子が好ましい。

【0041】本発明のインクジェット記録用紙の上記空隙層は皮膜としての特性を維持するために親水性バインダーを含有していることが必要である。

【0042】しかしながら、親水性バインダーの使用に当たっては、親水性バインダーが膨潤して、インクの初期の浸透時に膨潤して空隙を実質的に塞いでしまわないことが重要であり、この観点から比較的室温付近で膨潤性の低い親水性バインダーが好ましく用いられる。特に好ましい親水性バインダーは完全又は部分ケン化のポリビニルアルコール又はカチオン変性ポリビニルアルコールである。

【0043】ポリビニルアルコールの中でも特に好ましいのはケン化度が80以上の部分又は完全ケン化したものである。また、皮膜脆弱性を改良する観点から、ポリビニルアルコールの平均重合度は500～3500が好ましく、特に好ましくは1000～3500のものが用いられる。

【0044】また、カチオン変性ポリビニルアルコールとしては、例えば特開昭61-10483号に記載されているような、第1～3級アミノ基や第4級アンモニウム基を上記ポリビニルアルコールの主鎖又は側鎖中に有するポリビニルアルコールである。

【0045】また、前記空隙層中には他の親水性バインダーを含有させることが出来るが、好ましくはそれらの親水性バインダーは上記ポリビニルアルコール又はカチオン変性ポリビニルアルコールに対して概ね20重量%以下であることが好ましい。

【0046】次に本発明のインクジェット記録用紙の空隙層、特に支持体から離れた側の空隙層を形成する場合において、好ましく用いられる前記方法(2)及び(3)について、以下更に詳細に説明する。

【0047】前記方法(2)では、好ましくは空隙率を150容量%以上にするのがよい。空隙率の上限は、充填剤の種類や親水性バインダーの種類により一般に変化するが、皮膜としての強度や脆弱性等から一般には200容量%以下である。

【0048】空隙率を100容量%以上とするには、固体微粒子と親水性バインダーの比率が特に重要であり、この方法では該固体微粒子の親水性バインダーに対する重量比が10以上、200未満にすることが好ましい。この重量比が10未満では空隙容量が100%以上得ることが困難となり、200以上の場合には皮膜の脆弱性が劣化する。

【0049】この場合、特に前記の炭酸カルシウム微粒子、アルミナ又はアルミナ水和物微粒子を使用することが好ましい。

【0050】前記方法(3)は軟凝聚状態を形成して網目構造を皮膜中に形成する方法で、好ましくは親水性バインダーを含有する水溶液中に分散状態にある1次超微粒子が、接触点が比較的制限された状態でお互いに凝聚し合う状態を経由して形成される。このような軟凝聚状態は直線的もしくは分岐状に凝聚体を形成したものが水溶液中に分散された状態や、或いはこれらの凝聚体が更に凝聚し合って水溶液中で3次元網目構造をとる状態が含まれる。

【0051】何れの場合であっても、この水溶液を支持体上に塗布乾燥することによって、形成された皮膜中に微細な構造を形成することが出来る。

【0052】この様にして得られた皮膜中の微細な空隙の大きさは、概ね1次粒子の大きさからそれらの数倍程度の大きさであり、微細な大きさの空隙である特徴がある。

【0053】この様な軟凝聚状態を形成する方法としては、例えば1次粒子がお互いに凝聚しにくく、安定に存在できるような親水性ポリマーを含有する水溶液中に、粒子の凝聚を加速するような親水性ポリマーを極微量添加して僅かに凝聚を形成する方法、或いは1次粒子表面と弱い結合が出来るような水溶性ポリマーを有する水溶液中で形成される。

【0054】本発明では、特に、後者の方法が空隙の量を比較的コントロールしやすく安定に形成しやすいこと、使用する微粒子の量に比較してより多い空隙量が得られること、更には皮膜の光沢性がより高い皮膜が得られることから好ましい。

【0055】この場合特に好ましいのは前記微粒子シリカを1次粒子として使用し、親水性バインダーとしてポリビニルアルコール又はカチオン変性ポリビニルアルコールを用いる場合である。この場合、微粒子シリカ表面のシラノール基とビニルアルコールの水酸基が弱い水素結合を行い、軟凝聚体が形成される。

【0056】この様な微粒子シリカとしては特に気相法

と呼ばれる合成方法で合成された微粒子シリカが好ましく用いられる。

【0057】この方法で、親水性バインダーとして特に好ましく用いられるポリビニルアルコールの重合度は1000以上が好ましく、特に1500以上が皮膜にひび割れを起こさないようにするために好ましい。

【0058】ここで、ポリビニルアルコールと上記シリカの比率は、概ね1:10~1:1であり、好ましくは1:7~1:2の範囲である。

【0059】ポリビニルアルコールと微粒子シリカを用いて軟凝集体を含有する皮膜を形成する方法について以下に簡単に説明する。

【0060】pHを6~8、温度約40℃に保ったポリビニルアルコール水溶液(概ね5~15%)中に、シリカ分散液(概ね5~15%)を強攪拌しながら徐々に添加し、添加終了後に超音波分散機や高速ホモジナイザーなどにより分散する。この場合必要に応じて各種の界面活性剤を存在させてもよい。ついで、各種の添加剤を添加後、塗布に必要な目標粘度に調整して支持体上に公知の方法で塗布し乾燥することで上記空隙を有する皮膜が得られる。

【0061】本発明において、皮膜の脆弱性を改良するために各種の油滴を含有することが好ましいが、その様な油滴としては室温における水に対する溶解性が約0.01重量%以下の疎水性高沸点有機溶媒(例えば流動パラフィン、ジオクチルフタレート、トリクレジルホスフエート、シリコンオイル等)や重合体粒子(例えばステレン、ブチルアクリレート、ジビニルベンゼン、ブチルメタクリレート、ヒドロキシルエチルメタアクリレートなどの重合性モノマーを1種以上を重合させた粒子)を含有させることが出来る。その様な油滴は好ましくは親水性バインダーに対して10~50重量%用いることが出来る。

【0062】本発明のインクジェット記録用紙の空隙層の空隙容量の合計がインクジェット記録用紙1m<sup>2</sup>当たり20ml/m<sup>2</sup>以上である。空隙容量の合計が20ml/m<sup>2</sup>未満の場合、低インク量の吸収性は良好であるものの高いインク量の印字の際にインクが溢れて画質を低下させたり、或いは印字後の乾燥性が遅いなどの問題が発生しやすい。

【0063】一方、空隙容量の合計の上限は特に制限されないが、空隙層の乾燥膜厚は概ね50μm以下にすることがひび割れ等の皮膜の物理的特性を悪化させないために必要であることから概ね40ml/m<sup>2</sup>以下である。

【0064】従って、20ml/m<sup>2</sup>以上の空隙容量の合計を達成するためには空隙層の空隙率を100容量%以上にすることが好ましい。

【0065】ここで空隙容量とは、空隙層中の乾燥膜厚から空隙層中のバインダーや各種の充填剤等の固形分の

容量の総量を差し引いた値であり、空隙率はこれら固形分の容量に対する空隙量の割合を示す。

【0066】本発明においてはその効果に悪影響を与えない範囲で、膨潤性インク吸収層を設けても良い。この場合にはインク液滴に対して高い膨潤性を示すことが必要であるために、インク液膨潤性を示す親水性バインダーがこの膨潤層の主たる構成として用いられる。好ましく用いられる親水性バインダーとしては、例えば、ゼラチン又はゼラチン誘導体、ポリビニルピロリドン(平均分子量が約20万以上が好ましい)、プルラン、ポリビニルアルコール又はその誘導体、ポリエチレングリコール(平均分子量が10万以上が好ましい)、カルボキシメチルセルロース、ヒドロキシエチルセルロース、デキストラン、デキストリン、ポリアクリル酸及びその塩、寒天、 $\kappa$ -カラギーナン、 $\lambda$ -カラギーナン、 $\iota$ -カラギーナン、キサンテンガム、ローカストビーンガム、アルギン酸、アラビアゴム、プルラン、特開平7-195826号及び同7-9757号に記載のポリアルキレンオキサイド系共重合性ポリマー、水溶性ポリビニルピロリドン、或いは、特開昭62-245260号に記載のカルボキシル基やスルホン酸基を有するビニルモノマーの単独又はこれらのビニルモノマーを繰り返して有する共重合体等のポリマーを挙げることができる。これらの親水性バインダーは単独で使用しても良く、2種以上を併用しても良い。

【0067】膨潤層はインク液に対する早い浸透性及び膨潤性を有していることが必要なために、膨潤層の親水性バインダーとしては好ましくは、分子量が20万以上のポリビニルピロリドン、分子量が約5万以上のポリエチレンオキサイド、分子量が10万以上のポリエチレンオキサイドとポリプロピレンオキサイドの共重合体、ヒドロキシエチルセルロース、及びポリアクリルアミドから選ばれる少なくとも1種を含有する。

【0068】また、安定高速塗布の観点から、可逆的にゾルゲル変換可能な親水性バインダーを一部使用するのが好ましく、この点から、ゼラチン、ゼラチン誘導体、及び $\kappa$ -カラギーナンの少なくとも1種を使用するのが好ましい。

【0069】本発明において、各種の公知の界面活性剤を用いる事が出来る。インク液滴の拡がり度合いを比較的広くするためには一般に表面張力を下げる界面活性剤を使用するのが好ましく、なかでもアニオン系界面活性剤及びフッ素系界面活性剤を使用するのが好ましい。

【0070】本発明のインクジェット記録用紙の任意のインク受容性層中には、必要に応じて各種の添加剤を含有させることが出来る。

【0071】例えば、特開昭57-74193号、同57-87988号及び同62-261476号に記載の紫外線吸収剤、特開昭57-74192号、同57-87989号、同60-72785号、同61-1465

91号、特開平1-95091号及び同3-13376号等に記載されている退色防止剤、アニオン、カチオン又はノニオンの各種界面活性剤、特開昭59-42993号、同59-52689号、同62-280069号、同61-242871号及び特開平4-219266号等に記載されている蛍光増白剤、硫酸、リン酸、クエン酸、水酸化ナトリウム、水酸化カリウム、炭酸カリウム等のpH調整剤、消泡剤、デチレンギリコール等の潤滑剤、防腐剤、増粘剤、硬膜剤、帶電防止剤、マット剤等の公知の各種添加剤を含有させることもできる。

【0072】硬膜剤としては無機又は有機の硬膜剤を使用することが出来、例えばクロムみょうばん、ホルムアルデヒド、グリオキサール、エポキシ系化合物、ビニルスルホン系化合物、アクリロイル系化合物、s-トリアジン系化合物、N-メチロール系化合物、カルボジイミド系化合物、及びエチレンイミノ系化合物等を使用することが出来る。

【0073】本発明のインク記録面側の任意の構成層中には、画像の耐水化剤として特開昭56-84992号のポリカチオン高分子電解質、特開昭57-36692号の塩基性ラテックスポリマー、特公平4-15744号、特開昭61-58788号、同62-174184号等記載のポリアリルアミン、特開昭61-47290号記載のアルカリ金属弱酸塩等を一種以上用いることができる。

【0074】本発明のインクジェット記録用紙の支持体としては、従来インクジェット用記録用紙として公知のものを適宜使用できる。

【0075】透明支持体としては、例えば、ポリエステル系樹脂、ジアセテート系樹脂、トリアセテート系樹脂、アクリル系樹脂、ポリカーボネート系樹脂、ポリ塩化ビニル系樹脂、ポリイミド系樹脂、セロハン、セルロイド等の材料からなるフィルムや板、及びガラス板などを挙げられ、この中でもOHPとして使用されたときの輻射熱に耐える性質のものが好ましく、ポリエチレンテレフタレートが特に好ましい。このような透明な支持体の厚さとしては、約10~200μmが好ましい。

【0076】また、透明である必要のない場合に用いる支持体としては、例えば、一般的の紙、合成紙、樹脂被覆紙、布、木材、金属等からなるシートや板、及び上記の透光性支持体を公知の手段により不透明化処理したもの等を挙げることができるが、基紙の少なくとも一方に白色顔料等を添加したポリオレフィン樹脂被覆層を有する樹脂被覆紙（いわゆるRCペーパー）、ポリエチレンテレフタレートに白色顔料を添加してなるいわゆるホワイトペットが好ましい。支持体とインク受像層の接着強度を大きくする等の目的で、インク受容層の塗布に先立って、支持体にコロナ放電処理や下引処理等を行うことが好ましい。更に、本発明のインクジェット記録用紙は必ずしも無色である必要はなく、着色されたインクジェッ

ト記録用紙であってもよい。

【0077】これらの中でも本発明の支持体としては疎水性支持体が好ましく、例えばポリエチレンテレフタレート、ポリオレフィン樹脂被覆紙、ホワイトペットである。

【0078】本発明の無機微粒子を含有する層を支持体上に塗布する方法は公知の方法から適宜選択して行うことができるが、ロールコート法、ロッドバーコート法、エアナイフコート法、スプレーコート法、カーテンコート法或いは米国特許第2681294号公報記載のホッパーを使用するエクストルージョンコート法等が好ましく用いられる。

【0079】また、ゼラチンやゼラチン誘導体、 $\kappa$ -カラギーナン等の様なゾルゲル変換可能な親水性ペイントを用いる場合には、特開平6-64306号に記載されているように支持体上に塗布後、冷却してゲル状態にした後、コールドドライ法で乾燥する方法で行っても良い。

【0080】本発明のインクジェット記録用紙を用いて画像記録する際には、水性インクを用いた記録方法が用いられる。

【0081】本発明で言う水溶性染料を含有するインクジェット記録液（以下、単にインクジェット記録液ともいう。）とは、下記水溶性染料及び液媒体、その他の添加剤から成る記録液である。水溶性染料としてはインクジェットで公知の直接染料、酸性染料、塩基性染料、反応性染料或いは食品用色素等の水溶性染料が使用できる。

【0082】インクジェット記録液の溶媒としては、水及び水溶性の各種有機溶剤、例えば、メチルアルコール、イソプロピルアルコール、n-ブチルアルコール、tert-ブチルアルコール、イソブチルアルコール等のアルコール類；ジメチルホルムアミド、ジメチルアセトアミド等のアミド類；アセトン、ジアセトンアルコール等のケトン又はケトンアルコール類；テトラヒドロフラン、ジオキサン等のエーテル類；ポリエチレングリコール、ポリプロピレングリコール等のポリアルキレングリコール類；エチレングリコール、ブロピレングリコール、ブチレングリコール、トリエチレングリコール、1,2,6-ヘキサントリオール、チオジグリコール、ヘキシレングリコール、ジエチレングリコール、グリセリン、トリエタノールアミン等の多価アルコール類；エチレングリコールメチルエーテル、ジエチレングリコールメチル（又はエチル）エーテル、トリエチレングリコールモノブチルエーテル等の多価アルコールの低級アルキルエーテル類等が挙げられる。

【0083】これらの多くの水溶性有機溶剤の中でも、ジエチレングリコール、トリエタノールアミンやグリセリン等の多価アルコール類、トリエチレングリコールモノブチルエーテルの多価アルコールの低級アルキルエー

テル等は好ましいものである。

【0084】その他のインクジェット記録液の添加剤としては、例えばpH調製剤、金属封鎖剤、防カビ剤、粘度調整剤、表面張力調整剤、潤滑剤、界面活性剤及び防錆剤等が挙げられる。

【0085】インクジェット記録液はインクジェット記録用紙に対する濡れ性が良好にするために、20°Cにおいて、25~60dyn/cmが好ましく、より好ましくは30~50dyn/cmの範囲内の表面張力を有するのが好ましい。

【0086】本発明のインクジェット記録用紙を用いて画像記録する際のインク吐出方式は、インクジェット記録液を吐出可能なインクジェット記録方式であればよく、例えば「インクジェット記録技術動向」中村孝一編著（日本科学情報（株）、1995）p. 1~14に記載の連続噴射荷電制御方式やオンドマンド方式等の記録方式を用いることができる。しかし、これらの中でもオンドマンド方式の記録方式に適用して使用することにより、より大きな効果を得ることができる。

【0087】本発明におけるインク最大吐出量とは、本発明に用いるインクジェットプリンターが通常のあらゆる画像を出力する時に使用しうる単位体積当たりのイン

〔塗布液-1〕

純水

平均粒径約2.5μmの微粒子シリカ

平均重合度1700のポリビニルアルコール（ケン化度90%）

980ml

48.2g

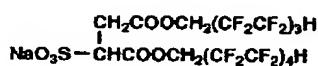
界面活性剤-1

24.1g

1.2g

【0091】

【化1】 界面活性剤-1



〔塗布液-2〕

純水

980ml

平均粒径約7nmの微粒子シリカ

48.2g

平均重合度3500のポリビニルアルコール（ケン化度90%）

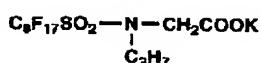
16.1g

1.2g

界面活性剤-2

【0094】

【化2】 界面活性剤-2



【0095】次に、インクジェット記録用紙-1において、〔塗布液-1〕及び〔塗布液-2〕を用いた各々塗布液を以下のように変更したインクジェット記録用紙-

ク体積量の最大値である。例えばカラー画像用のプリンターの場合、イエロー、マゼンタ、シアン、ブラック各単色の最高濃度を得るためにインク量を足し合わせたものが必ずしもインク最大吐出量ではない。インク最大吐出量は、インクジェット記録液1滴の体積が既知で、画像を形成するための液滴の配列方法が既知であれば計算によって求めることができる。

【0088】

【実施例】以下に本発明の実施例を挙げて説明するが、本発明はこれらの例に限定されるものではない。なお、実施例中で「%」は特に断りのない限り絶乾重量%を示す。

【0089】実施例1

100g/m<sup>2</sup>の原紙両面をポリエチレンで被覆した紙支持体（厚さ140μm、記録面側のポリエチレン層中に7重量%のアナターゼ型二酸化チタン含有し、記録面の裏面側にバック層としてアルカリ処理ゼラチン1.2g/m<sup>2</sup>と硬膜剤を含有する層を有する）上の記録面側に、下記の〔塗布液-1〕を湿潤膜厚が125μmに成るよう塗布し乾燥した。

【0090】

【0092】ついでこの塗布層の上に以下の組成の塗布液-2を湿潤膜厚100μmで塗布し乾燥して本発明のインクジェット記録用紙-1を得た。このようにして得られた皮膜の空隙容量の合計は24ml/m<sup>2</sup>であった。

【0093】

2~10をインクジェット記録用紙-1と同様にして作成した。

【0096】インクジェット記録用紙-2：〔塗布液-2〕の塗布を行わず、〔塗布液-1〕のみで湿潤膜厚125μmで2回塗布を行った以外はインクジェット記録用紙-1と同じ。（空隙容量の合計=約25ml/m<sup>2</sup>）

インクジェット記録用紙-3：〔塗布液-1〕の湿潤膜厚を80μm、〔塗布液-2〕の湿潤膜厚140μmで

塗布を行った以外はインクジェット記録用紙-1と同じ。（空隙容量の合計=約24m<sup>1</sup>/m<sup>2</sup>）

インクジェット記録用紙-4：〔塗布液-1〕の平均粒径2.5μmのシリカの代わりに平均粒径1.4μmのシリカを使用した以外はインクジェット記録用紙-1と同じ。（空隙容量の合計=約23m<sup>1</sup>/m<sup>2</sup>）

インクジェット記録用紙-5：〔塗布液-1〕の平均粒径2.5μmのシリカの代わりに平均粒径0.1μmのコロイド状シリカを使用した以外はインクジェット記録用紙-1と同じ。（空隙容量の合計=約21m<sup>1</sup>/m<sup>2</sup>）

インクジェット記録用紙-6：〔塗布液-1〕の界面活性剤を2、〔塗布液-2〕の界面活性剤を1に変え、

〔塗布液-2〕を塗布した後〔塗布液-1〕を塗布した以外はインクジェット記録用紙-1と同じ。（空隙容量の合計=約24m<sup>1</sup>/m<sup>2</sup>）

インクジェット記録用紙-7：〔塗布液-1〕及び〔塗布液-2〕の湿潤膜厚を何れも80μmで行った以外はインクジェット記録用紙-1と同じ。（空隙容量の合計=約16m<sup>1</sup>/m<sup>2</sup>）

インクジェット記録用紙-8：〔塗布液-1〕の平均粒径2.5μmの微粒子シリカの替わりに平均粒径8μmも微粒子シリカを使用した以外はインクジェット記録用紙-1と同じ。（空隙容量の合計=約23m<sup>1</sup>/m<sup>2</sup>）

インクジェット記録用紙-9：〔塗布液-1〕の平均粒径2.5μmの微粒子シリカの替わりに平均粒径12μmも微粒子シリカを使用した以外はインクジェット記録用紙-1と同じ。（空隙容量の合計=約24m<sup>1</sup>/m<sup>2</sup>）

インクジェット記録用紙-10：〔塗布液-2〕の平均粒径7nmも微粒子シリカの替わりに平均粒径50nmのコロイド状シリカを使用した以外はインクジェット記録用紙-1と同じ。（空隙容量の合計=約23m<sup>1</sup>/m<sup>2</sup>）

得られた各々のインクジェット記録用紙について、セイコーエプソン株式会社製インクジェットプリンターMJ-5100Cを用い、評価パターンを印字し以下の項目の評価を行った。

#### 【0097】(1) インク吸収容量：

記録用紙	インクジェット		インク吸収容量	インク吸収性	乾燥性	ドット直径		光沢度
	①	②				K	K/Y	
1 (本発明)	○	○	0.09	2分	80	110	66	
2 (比較例)	○	○	0.06	1分	100	150	5	
3 (本発明)	○	○	0.10	2分	80	110	67	
4 (本発明)	○	○	0.10	2分	90	110	70	
5 (比較例)	○	△	0.13	3分	90	130	72	
6 (比較例)	○	○	0.07	1分	100	140	8	
7 (比較例)	△	×	0.18	4分	60	(a)	68	
8 (本発明)	○	△	0.09	2分	80	110	60	
9 (本発明)	○	○	0.09	2分	80	110	51	
10 (本発明)	○	○	0.11	2分	90	110	68	

(a) 測定不能

①イエローとシアンの各インクの最大インク量の60%の吐出時

②イエローとシアンの各インクの最大インク量の60%の吐出とマゼンタインクの最大インク量の30%を吐出させた時、各々の場合のインクの溢れの状態を目視で観察した。

#### 【0098】[インクの溢れ]

○：印字直後に全く溢れない

△：印字直後には僅かに溢れているが約10秒以内に乾燥する

×：印字直後に溢れており表面が乾燥するのに10秒以上かかる。

#### 【0099】(2) インク吸収性：

①イエロー及びシアンのそれぞれ最大インク量の30%になるように均一に吐出させて記録し、ベタ部の赤色反射濃度をマイクロデンシトメーター（アパーーチュア=200μmφ）を用いて20点測定し、その濃度のバラツキの標準偏差を求め平均反射濃度で割った値を求めた。

20 インク吸収性が良好な場合には画像にムラが無くこの値が小さくなるが、インク吸収性が低下するとこのお互いのインク液滴同士がインクジェット記録紙上で互いにビーディングを起こしてムラになりこの値が増加する。

【0100】(3) 乾燥性：イエローとマゼンタの60%印字部を印字後一定時間経過後、普通紙を重ねて放置し、インクが普通紙に転写しなくなるまでの時間を求めた。

30 【0101】(4) ドット直径：ブラックインクの單一ドット直径(K)及び、イエローべタ印字部にブラックの單一ドットを印字しその直径を顕微鏡で観察して求めた(K/Y)。直径は、それぞれ20個のドットの面積を測定しこれを円換算したときの直径の平均値として求めた。(単位:μm)

(5) 光沢度：印字面を日本電色工業株式会社製変角光沢度計(VGS-1001DP)を用いて75度光沢を測定した。

【0102】得られた結果を表1に示す。

【0103】

【表1】

【0104】表1の結果から、本発明のインクジェット記録用紙-1、3、4、8は高いインク吸収容量、良好なインク吸収性と乾燥性並びに高い光沢性を有し、かつ、ドットサイズが小さく高品位な画像は得られる。これに対して、支持体より離れた側に平均粒径の大きな微粒子を用いたインクジェット記録用紙-6や平均粒径の大きな微粒子のみを用いたインクジェット記録用紙-2はインク吸収性や乾燥性は良好であるが、光沢性が大幅に低下し、しかもドットサイズが広く、インク液滴を微小化しても高品位な画像が得にくい。

【0105】支持体に近い側に、支持体に遠い側の微粒子の平均粒径の小さな微粒子を用いたインクジェット記録用紙-5はインク吸収性の低下がみられる。インクジ

## 〔塗布液-2a〕

純水

微粒子炭酸カルシウム (平均粒径=約0.03μm)

平均重合度1700のポリビニルアルコール (ケン化度90%)

## 界面活性剤-1

また、〔塗布液-2a〕の平均粒径0.03μmの微粒子炭酸カルシウムの替わりに平均粒径0.07μmの微粒子炭酸カルシウムを使用した以外はインクジェット記録用紙-21と同様にしてインクジェット記録用紙-28を作成した。

【0109】各々のインクジェット記録用紙の空隙用と膨潤層膜厚は以下の通りであった。

【0110】インクジェット記録用紙-21:空隙容量の合計=約26ml/m<sup>2</sup>

インクジェット記録用紙-22:空隙容量の合計=約25ml/m<sup>2</sup>

インクジェット記録用紙-23:空隙容量の合計=約25ml/m<sup>2</sup>

インクジェット記録用紙-24:空隙容量の合計=約2

記録用紙	インクジェット		インク吸収性	乾燥性	ドット直径		光沢度 (%)
	①	②			K	K/Y	
21(本発明)	○	○	0.11	2分	90	110	68
22(比較例)	○	○	0.06	1分	100	150	5
23(本発明)	○	○	0.12	2分	90	110	72
24(本発明)	○	○	0.12	2分	90	110	71
25(比較例)	○	△	0.14	3分	90	120	74
26(比較例)	○	○	0.07	1分	100	140	9
27(比較例)	○	△	0.19	4分	60	(a)	68
28(本発明)	○	○	0.13	3分	90	120	61

(a) 測定不能

【0112】表2の結果から、無機充填剤として、微粒子シリカに換えて微粒子炭酸カルシウムに置き換えるても実施例1同様の効果が得られることがわかる。

## 【0113】実施例3

実施例1において、〔塗布液-2〕を以下の〔塗布液-2b〕

エット記録用紙-7は空隙容量の合計が小さくインク吸収容量が足りず高品位な画像は得られなかった。

【0106】また本発明の好ましい態様であるインクジェット記録用紙に含有される微粒子より大きい平均粒径の大きな微粒子を用いた本発明のインクジェット記録用紙-9、10は、本発明の好ましい態様であるインクジェット記録用紙にひして、光沢性が若干低い。

## 【0107】実施例2

実施例1において、〔塗布液-2a〕を以下の〔塗布液-2a〕に変更した以外は実施例1と同様にしてインクジェット記録用紙-1~7と同様構成のインクジェット記録用紙-21~27を作成し、実施例1と同様にして評価した。

## 【0108】

9.60ml

76.9g

9.6g

1.2g

5ml/m<sup>2</sup>インクジェット記録用紙-25:空隙容量の合計=約23ml/m<sup>2</sup>インクジェット記録用紙-26:空隙容量の合計=約26ml/m<sup>2</sup>インクジェット記録用紙-27:空隙容量の合計=約19ml/m<sup>2</sup>インクジェット記録用紙-28:空隙容量の合計=約25ml/m<sup>2</sup>

30 各のインクジェット記録用紙を実施例1と同様な評価を行い、結果を表2に示す。

## 【0111】

## 【表2】

2b]に変更した以外は実施例1と同様にしてインクジェット記録用紙-1~7と同様構成のインクジェット記録用紙-31~37を作成し、実施例1と同様にして評価した。

## 【0114】

